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THE UNIVERSITY OF ALBERTA

SOME CARBENE COMPLEXES OF MANGANESE AND RHENIUM

by

©

MICHAEL JOHN WEBB

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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OF DOCTOR OF PHILOSOPHY

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled SOME CARBENE COMPLEXES OF MANGANESE AND RHENIUM submitted by Michael John Webb in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

The reaction of the appropriate complex of the type $R_3M'M(CO)_5$ with methyllithium, followed by treatment with aqueous hydrochloric acid yielded cyclic germoxy- and stannoxy-carbene complexes of empirical formula $R_2M'M(CO)_4COMe$ (R = Ph; M' = Ge; M = Mn, Re. R = Me; M' = Ge, Sn; M = Re. R = Me; M' = Ge; M = Mn). ^{13}C NMR spectroscopy has been important in the formulation of these derivatives as carbene complexes.

Through the use of ^{1}H NMR spectroscopy, two of the cyclic germoxycarbene complexes (R = Me; M = Mn, Re) have been found to exist as equilibrium mixtures of monomeric and dimeric forms in solution. Thermodynamic parameters for these equilibria have been determined.

In several reactions of germoxycarbene complexes with methyllithium and methoxide ion it appeared that nucleophilic attack occurred at the germanium atom, causing ring opening to occur and providing a route to the formation of non-cyclic carbene complexes.

The reaction of complexes of the type $R_3M'M(CO)_5$ with methyl- or phenyl-lithium, followed by treatment with aqueous Et_3OBF_4, yielded a series of non-cyclic carbene complexes, *cis*-$R_3M'M(CO)_4C(OEt)R'$ (R = Ph; M' = Ge, Sn; M = Mn; R' = Me, Ph. R = Me; M' = Ge; M = Re; R' = Me).

The reactions of two such derivatives with ethylamine led to the aminocarbene complexes, *cis*-$R_3GeM(CO)_4C(NHEt)Me$ (R = Ph; M = Mn. R = Me; M = Re), both of which appeared to be formed as a mixture of two isomers, resulting from restricted rotation about the carbene carbon to nitrogen bond.

A ^{13}C NMR study has been carried out of a complex containing a ketone group bound to rhenium through its oxygen atom. The assignment of the ketonic carbon resonance was confirmed through the use of a ^{13}C enriched sample.

^{13}C studies have been extended to include a series of rhenium pentacarbonyl derivatives. Earlier attempts to correlate ^{13}C chemical shifts of carbonyl carbon atoms with carbonyl stretching force constants have been examined in the light of the new data, and the conclusion has been reached that this type of correlation is inadequate to explain many spectral features.

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The author wishes to express his indebtedness and gratitude to:

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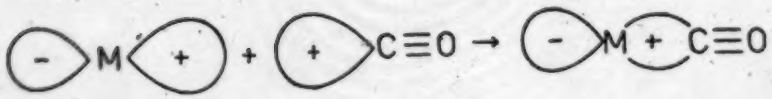
CHAPTER I

Transition Metal Carbonyl Complexes

Transition metal carbonyls have been known since the discovery of $Ni(CO)_4$ by Mond in 1890.[1] However, a systematic study of the chemistry of these organometallic derivatives did not begin until recent years and this has rapidly become a very active area of research. Many derivatives of metal carbonyls have been prepared and some complexes have found use as catalysts in industrial processes. A useful guide to the literature in organo-transition metal chemistry covering the years 1950-1970 has been published.[2] Other useful general reviews include a "Specialist Periodical Report" on "Organometallic Chemistry,"[3] and the "MTP International Review of Science, Series One,"[4] covering inorganic chemistry.

Transition metal carbonyl complexes generally involve a metal in a low formal oxidation state. The strong metal-carbon bonds in these derivatives have been attributed to the synergic effect of σ and π interactions.[5,6] A simplified molecular orbital picture of this type of bonding is shown in 1 and 2. A metal carbon σ bond is formed by overlap of a filled sp-hybrid orbital of carbon and a vacant hybrid orbital of the metal in 1. In addition a π bond is formed by overlap of a filled d orbital of the



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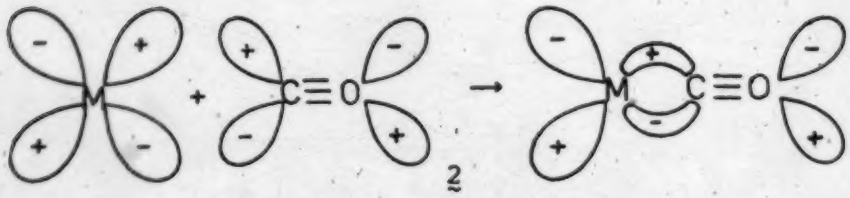


2

metal with an empty, antibonding π* orbital of the CO group in 2. Charge transfer in the σ bond is in the opposite direction to that in the π bond, and the latter is crucial in removing excess negative charge from the metal atom. The increase in electron density in the π* antibonding orbital of CO reduces the CO bond order. This effect is readily observed in infrared spectroscopy; the stretching frequency of free CO is 2155 cm^{-1}, but in metal carbonyl complexes CO stretching bands are usually found below 2100 cm^{-1}. Similar synergic bonding pictures can be constructed for ligands which are often found as substituents in carbonyl derivatives and which can also contribute to the stabilization of the metal in a low oxidation state, for example, tertiary phosphines, nitric oxide and various olefins.

Attempts have been made to estimate the relative contributions of the σ-donor and π-acceptor properties of a given ligand to the strength of the metal-ligand bond, and this has been a point of some controversy. In carbonyl complexes the discussion has largely involved the use of infrared spectroscopy,[7,8] although other approaches have been used.[9] The interdependence of the σ and π contributions expected from the synergic bonding model suggests that bonding discussions should acknowledge the importance of both.

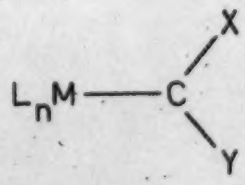
Most transition metal carbonyls and their derivatives are diamagnetic, and their stoichiometry can often be predicted by the very useful effective atomic number rule, also known as the "noble gas formalism."[10] This requires that the number of electrons possessed by the transition metal plus the number of electrons contributed to the metal by the ligands equals the number of electrons in the succeeding noble gas atom. Ligands such as carbon monoxide and carbene groups are thought of as two electron donors. Main group IV ligands, such as the Me_3Ge- group, covalently bound to the metal act as one electron donors. As an illustration of the noble gas formalism consider the carbene complex *cis*-$Me_3GeRe(CO)_4C(OEt)Me$ described later in this work. A rhenium atom requires eleven electrons from the ligands to attain the electronic configuration of radon.

These electrons are supplied as follows: eight from the four carbonyl ligands, two from the carbene ligand and one from the organogermanium group.*

A number of transition metal complexes, notably many of rhodium, iridium, palladium and platinum do not conform to the effective atomic number rule. However, the general usefulness of the rule in a vast majority of other cases cannot be overemphasised. All of the novel complexes of manganese and rhenium reported later in this thesis conform to the effective atomic number rule.

Transition Metal Carbene Complexes

The term transition metal carbene complex will be used here to describe compounds of the general type shown in 3. The carbene :CXY is coordinated to a metal atom, M,



3

*This assumes that the rhenium atom is formally in the zero oxidation state. Group IV ligands can also be thought of as anionic two electron donors to rhenium in the +1 oxidation state; Re(+1) requires twelve electrons to attain the radon configuration and hence the effective atomic number rule is obeyed.

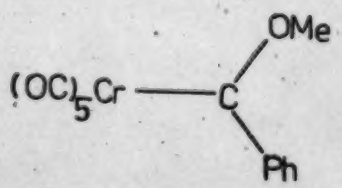
with other ligands, L_n, also present. The carbene ligand is usually bound terminally but can also act as a bridging moiety in which case the carbon atom is no longer three coordinate. Examples of this latter type will not be discussed here. The stability of transition metal carbene complexes of the type 3 illustrates how coordination to a metal can stabilize groups which would normally not be isolable in an uncomplexed state.

Since the existence of transition metal carbene complexes was established with the preparation of $W(CO)_5C(OMe)Ph$ and $W(CO)_5C(OMe)Me$[11] in 1964, this research area has received much attention. Several useful reviews exist[12-15] and no attempt will be made here to review the very large amount of work published to date. Some aspects of carbene chemistry relevant to this thesis should however be discussed.

Carbene ligands are usually found in complexes in which the metal is in a low oxidation state. These complexes therefore often contain such groups as carbon monoxide and tertiary phosphines as accompanying ligands. With few exceptions stable carbene complexes have been obtained when X or Y, or both, in 3 contain an element other than carbon, usually oxygen, nitrogen or sulphur, bound directly to the carbene carbon atom. The π interaction between the carbene carbon and adjacent heteroatoms is very

important in the stabilization of most carbene complexes. A recent, and very interesting example of a carbene in which such a heteroatom is not present is the compound $W(CO)_5CPh_2$,[16] a stable complex containing a diphenylcarbene group. Terminal diphenylcarbene complexes of rhodium had earlier been postulated,[17] but the complexes have since been shown to contain only bridging diphenylcarbene groups.[18] The carbene complexes synthesised in this work all involve heteroatom stabilization of the carbene and the following brief bonding discussion applies to derivatives of this general type.

A clear and concise account of the bonding in metal carbene complexes has appeared elsewhere;[14] only a short summary of the more important features will therefore be presented here. This can perhaps best be achieved by reference to a particular example, namely, $Cr(CO)_5C(OMe)Ph$,[19] **4**.



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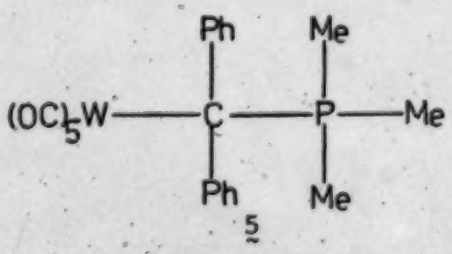
In this complex the three atoms bound directly to the carbene carbon atom are coplanar and bond angles at the carbene carbon of 122°, 104°, and 134° establish the essentially sp^2 character of this atom. The carbene carbon to oxygen bond length of 1.33 Å is very much shortened compared with a normal C-O single bond distance (~ 1.43 Å) reflecting the $p\pi$-$p\pi$ overlap involving lone pair electron density on oxygen and the empty p orbital of the carbene carbon atom. The phenyl ring is approximately perpendicular to the plane defined by the carbene carbon and the three atoms directly bound to it, suggesting that no π overlap occurs between the phenyl ring and carbene carbon atom.

The bonding of the carbene to the metal atom can be discussed in similar synergic bonding terms previously used to describe bonding between a metal and a carbonyl group (see 1 and 2). The carbene carbon atom can be thought to donate a pair of electrons from an sp^2 hybridised orbital into a vacant hybridised orbital of the metal and to receive metal d electrons into its empty p orbital. Thus the carbene carbon atom is π bonded to both its heteroatom and the transition metal, in this case oxygen and chromium. The observed chromium to carbene distance of 2.04 Å in $Cr(CO)_5C(OMe)Ph$ is appreciably shorter than that predicted for $Cr\text{-}C(sp^2)$ of 2.21 Å, using an estimated Cr(0) covalent

radius of 1.48 Å.[20] Thus some degree of π bonding between the metal and the carbene is indicated. It appears that the π-acceptor/σ-donor ratio is lower for a carbene than for a carbonyl group from force constant analyses. For example, approximate force constants for the carbonyl groups *cis* and *trans* to the carbene ligand in $Cr(CO)_5C(OMe)Ph$ are 15.93 and 15.76 mdyn/Å respectively.[21] The lower force constant for the *trans* carbonyl fully supports the above contention.

Despite π bonding from both the metal and heteroatom attached to a carbene carbon atom, the latter still behaves chemically as an electrophile. For example, phenyllithium attacks the carbene carbon in $W(CO)_5C(OMe)Ph$ in the first stage of the synthesis of the diphenylcarbene derivative mentioned earlier.[16] This latter compound, $W(CO)_5CPh_2$ has itself been reacted with the nucleophile trimethylphosphine to give a complex formulated as an ylide,[22] 5. Similar



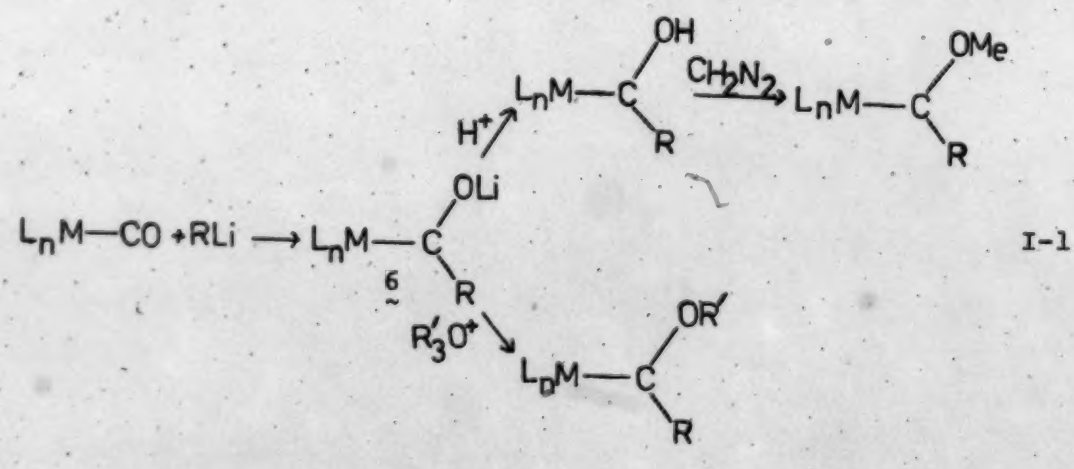
5

derivatives have been prepared from carbene complexes of chromium and tungsten in which oxygen or sulphur heteroatoms are present in the carbene ligands.[23,24] The

electron-deficient nature of coordinated carbene carbon atoms is further exemplified by their very low field chemical shifts in ^{13}C NMR spectra. For example, the carbene carbon resonance in $Cr(CO)_5C(OMe)Ph$ occurs at -350.93 p.p.m. downfield from tetramethylsilane.[21]

Most of the general methods of synthesis of carbene complexes, of which there are now quite a few, have been described elsewhere,[14] and no attempt to describe all of these methods will be made here. Only two methods of synthesis of new carbene complexes are employed in this work and these will now be described.

Fischer and Maasböl[11] found that organolithium reagents attack coordinated carbonyl groups to give acylate



I-1

intermediates of the type 6. Such intermediates can be converted to neutral carbene derivatives by treatment with trialkyloxonium salts,[25] or by protonation to give a

hydroxycarbene complex followed by treatment with diazomethane[11] as shown in I-1. In this work both protonation and alkylation of acylate salts have been carried out, the former producing some rather unexpected and interesting results (see Chapter II).

The second route to new carbene complexes employed herein involves the modification of carbene ligands already coordinated to a metal. Fischer and co-workers discovered that alkoxy groups can be cleaved from carbene carbon atoms by treatment with reagents such as amines[26] and thiols.[12]

$$(OC)_5CrC(OMe)Me + MeNH_2 \rightarrow (OC)_5CrC(NHMe)Me + MeOH \qquad \text{I-2}$$

$$(OC)_5CrC(OMe)Ph + PhSH \rightarrow (OC)_5CrC(SPh)Ph + MeOH \qquad \text{I-3}$$

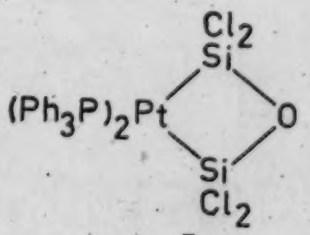
It seems appropriate here to present a brief description of attempts to synthesize analogs of carbene complexes containing elements other than carbon from the fourth main group, namely, silylene, germylene, stannylene and plumbylene complexes. Such derivatives should be discussed since complexes which have been claimed to belong to this class are relevant to structural arguments concerning the cyclic compounds described in Chapter II.

In 1970, Schmid and Balk[27] claimed to have prepared a silylene complex of platinum according to the following scheme:

$$(Ph_3P)_4Pt + Si_2Cl_6 \rightarrow cis\text{-}(Ph_3P)_2Pt(SiCl_3)_2 + 2PPh_3 \qquad \text{I-4}$$

$$cis\text{-}(Ph_3P)_2Pt(SiCl_3)_2 + PPh_3 \rightarrow (Ph_3P)_2Pt(SiCl_2)_2 + Cl_2PPh_3 \qquad \text{I-5}$$

The analogous bisdibromosilylene complex was also claimed. This work has since been contested[28] and the product of I-5 reported by Schmid and Balk reformulated as the siloxane complex, 7.



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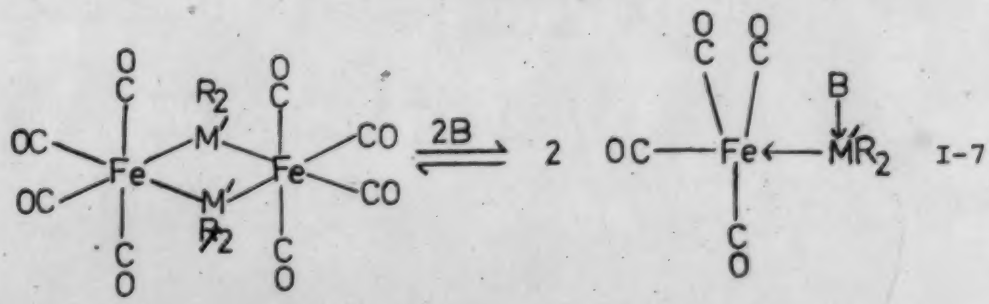
Much of the subsequent interest in this area has been generated by the work of T. J. Marks and co-workers. It was found that the reactions of dialkylgermanium- and dialkyltin-dihalides with $Na_2Cr_2(CO)_{10}$ in THF proceed as shown in I-6.[29]

$$R_2M'X_2 + Na_2Cr_2(CO)_{10} \xrightarrow{THF} R_2M'(THF) + Cr(CO)_5 + NaCl + NaCr(CO)_5Cl \qquad \text{I-6}$$

8

R = Me, M' = Ge; R = Me, M' = Sn; R = *t*-Bu, M' = Sn.

The product is drawn here as represented in the original publication in which derivatives of this type were referred to as germylene and stannylene complexes. It was found that the THF could not be removed from the product without inducing decomposition and attempts to carry out the reaction in non-coordinating solvents failed. Thus the germanium and tin atoms in these complexes did not exist in a three coordinate environment. Similar products have been prepared from the reactions of Lewis bases with molecules of the general formula $[R_2M'Fe(CO)_4]_2$,[30] 9.

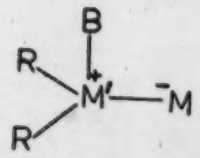


9 10

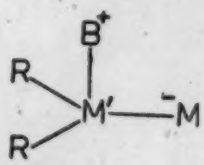
M' = Ge, R = Me, Ph; M' = Sn, R = Me, *t*-Bu, Ph; M' = Pb, R = *n*-Bu, Ph. B = THF, pyridine, acetone, acetonitrile, diethyl ether, dimethylformamide.

Subsequent work has suggested that compounds of the type 8 and 10 are not true carbene analogs. A crystal structure of a complex of type 8, in which R = *t*-Bu, M' = Sn and the Lewis base coordinated to the tin atom

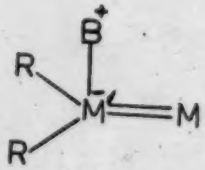
was pyridine, clearly revealed a coordination number of four for the tin atom and a valence shell octet of electrons.[31] On the basis of ^{119}Sn Mössbauer and X-Ray Photoelectron (ESCA) studies of complexes of the types 8 and 10 it was concluded that these molecules are better described as ylide derivatives,[32] with contributions from



11a



11b

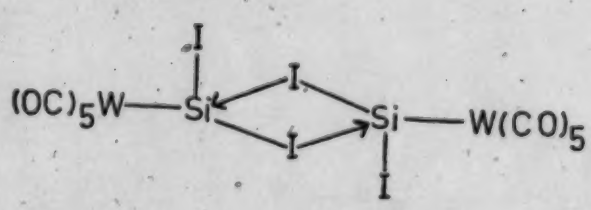


11c

structures 11a-c. This is fully consistent with solution infrared studies of derivatives of this type, the carbonyl stretching bands normally occurring in regions generally associated with anionic metal carbonyl species.[29,30] It should be noted here that carbene complexes containing heteroatoms such as oxygen and nitrogen gain stability by the donation of electron density from the heteroatom to the carbene carbon atom. This can be viewed in terms of the type of resonance structures shown in 11a-c[15] with the difference that this stabilization is within the carbene ligand itself and does not require the coordination number at carbon to increase from three to four.

Ylide complexes related to the compounds prepared by Marks[29,30] have been prepared by the direct interaction of a nitrogen-germanium ylide, 3-benzothiazole-dichlorogermylene, with the hexacarbonyls of chromium, molybdenum and tungsten under ultraviolet irradiation, giving complexes of the type $C_7H_5NS \cdot GeCl_2M(CO)_5$.[33]

Schmid and Boese[34] discovered that the reaction of $W(CO)_6$ with Si_2I_6 under ultraviolet irradiation in *n*-pentane yields dimeric "pentacarbonyl(diiodosilylene)tungsten(0)," $[(CO)_5WSiI_2]_2$. The dimeric nature of the complex was clearly established by mass spectrometry and a solution molecular weight determination in benzene. It was found that the solvent THF would cleave the bridges to give monomeric THF adducts analogous to Marks' compounds.[29,30] The dimeric $[(CO)_5WSiI_2]_2$ complex was postulated to contain iodine bridges leading to the structure 12. If this structure is



12

correct the complex can be considered as formally analogous to those of Marks[29,30] with stabilization arising from donation of lone pair electron density from the bridging iodine atoms.

Inconclusive results have appeared regarding the reaction of tin dihalides and the complex $CsGeCl_3$ with hexacarbonyls of chromium, molybdenum and tungsten under untraviolet irradiation in THF.[35] The complexes were formulated as monomeric $M(CO)_5SnX_2$ (X = Cl, Br, I) and $M(CO)_5GeCl_2$. Some of these complexes existed as THF adducts and others did not. In the latter case the complexes were described as having the Group IV atom with coordination number three. Solution infrared spectra and solution molecular weight determinations were carried out in the powerfully coordinating solvents CH_3CN and THF respectively, both of which might be suspected of breaking up larger polymeric units. Furthermore mass spectra of these complexes could not be obtained which could also be consistent with polymeric units, presumably linked by halogen bridges.

Other inconclusive work postulating silylene-, germylene and stannylene-transition metal derivatives as reaction intermediates has appeared.[36,37] The reactions under discussion involve the replacement of chlorine atoms on the coordinated Group IV ligand with fluorine atoms, by interaction with reagents such as $AgBF_4$ as in I-8. There

$$ClPh_2GeMn(CO)_5 + AgBF_4 \rightarrow FPh_2GeMn(CO)_5 + AgCl + BF_3 \qquad \text{I-8}$$

is no mechanistic evidence however to establish whether the reaction involves a three- or five-coordinate intermediate.

Elegant work by Lappert and co-workers has produced the first fully-authenticated transition metal stannylene complexes. A stable divalent tin species was synthesised (I-9) and reacted with chromium and molybdenum hexacarbonyls to give stable stannylene complexes (I-10).[38] The X-ray

$$SnCl_2 + (Me_3Si)_2CHLi \xrightarrow[0°]{\text{ether}} Sn[CH(SiMe_3)_2]_2 \qquad \text{I-9}$$

$$M(CO)_6 + Sn[CH(SiMe_3)_2]_2 \xrightarrow[20°,\ h\nu]{n\text{-hexane}} [(Me_3Si)_2CH]_2SnM(CO)_5 \qquad \text{I-10}$$

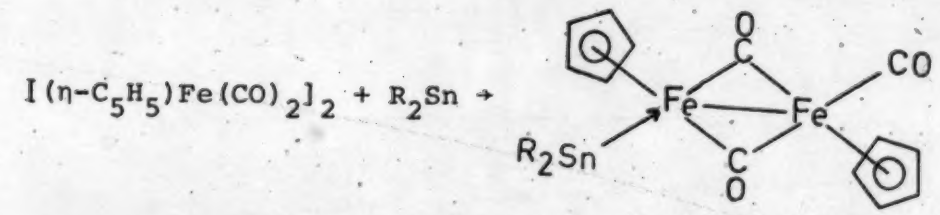
M = Cr, Mo

crystal structure of the chromium complex confirms the stannylene formulation,[39] and other stannylene complexes have been prepared using the same tin(II) ligand (I-11-14).

$$(Ph_3P)_3RhCl + R_2Sn \rightarrow (Ph_3P)_2(R_2Sn)RhCl \qquad \text{I-11}$$

$$[(Et_3P)PtCl_2]_2 + R_2Sn \rightarrow (Et_3P)PtCl(SnR_2)(SnR_2Cl) \qquad \text{I-12}$$

$$(\text{norbornadiene})Mo(CO)_4 + 2R_2Sn \rightarrow \textit{trans}\text{-}(R_2Sn)_2Mo(CO)_4 \qquad \text{I-13}$$

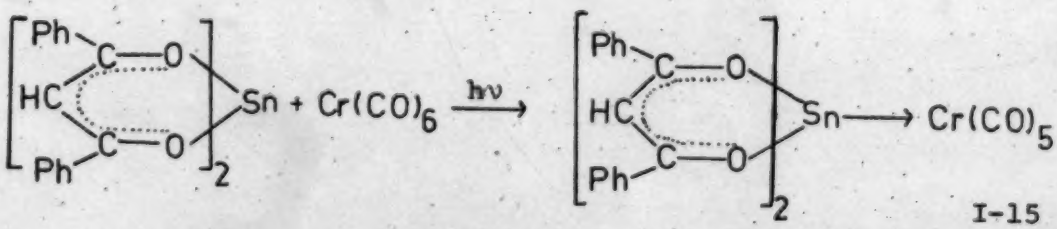


I-14

13

The novel plumbylene complex $[(Me_3Si)_2CH]_2PbMo(CO)_5$ has also been prepared.[39] It is thought that the stability of these transition metal complexes and of the parent tin(II) and lead(II) ligands is probably kinetic in origin and derives from the bulky R groups.[39]

Recently Harrison *et al.* have reported reactions analogous to I-7 involving the reaction of pyridine with $[R_2M'Fe(CO)_4]_2$ derivatives (where R = Cl, Br, C_5H_5, MeC_5H_4, and several β-diketonate ligands).[40] Reactions of the type I-15 and I-16 were also reported. Both reactions formally



I-15

14

involve tin(II) species. The product of reaction I-15, 14, clearly contains five coordinate tin and little data was given regarding the product of I-16.

$$(C_5H_5)_2Sn + W(CO)_6 \xrightarrow{h\nu} (C_5H_5)_2SnW(CO)_5 \qquad \text{I-16}$$

From the above description it can be seen that the only fully authenticated carbene analogs produced to date are those of Lappert *et al.*,[38,39] in which the Group IV atom is three coordinate. Unfortunately, the terms "stannylene" etc. have also been used to describe the four coordinate compounds prepared by Marks and others.[29,30] It might avoid confusion if these latter derivatives were described as analogs of ylide complexes; this has been shown to be a rather appropriate description of the bonding.[32] Thus the complex $[C_5H_5N(t\text{-}C_4H_9)_2SnCr(CO)_5]$[31] would be renamed (pyridino-di-tert-butylstannylide)pentacarbonylchromium.

Complexes with Main Group IV Metals

Over the past decade this research area has received much attention and many transition metal complexes containing silicon, germanium, tin and lead moieties as ligands have been prepared. One small area of this work, namely, approaches to the synthesis of metal carbene analogs, has been described above. Several general reviews have appeared of which two of the more recent and useful examples are those of Glockling and Stobart,[41] and Brooks and Cross.[42] Also there exists a review of transition metal-silicon compounds.[43]

The bonding between transition metals and elements of the fourth main group other than carbon is usually thought to consist of a σ and π bond combination, the latter involving donation of d electron density from the metal into an empty d orbital on the ligand. It appears from attempts to correlate CO stretching frequencies or force constants with σ and π bonding within the transition metal-group IV metal bond that the σ bonding predominates.[8,44] The π character appears to be appreciable when halogen substituents are attached to the group IV atom, thus increasing its electronegativity with respect to the transition metal. This has been shown by ^{119}Sn Mössbauer[45] and ^{59}Co NQR[46] experiments, as well as by molecular orbital calculations.[47]

Of relevance to the formation of the cyclic derivatives discussed in Chapter II is the reactivity of group IV ligands attached to a transition metal, more specifically the conditions under which alkyl and aryl substituents have been cleaved from germanium and tin atoms coordinated to manganese and rhenium. Of particular interest are the reactions involving hydrogen halides, the reagents also employed in this work, and some examples are given below.

$$Ph_3SnMn(CO)_5 + \text{excess } HCl \xrightarrow[0\text{-}5^\circ]{CCl_4}$$

$$PhCl_2SnMn(CO)_5 + (\text{trace})Cl_3SnMn(CO)_5 \qquad {}^{48}\text{I-17}$$

$$Me_3SnMn(CO)_5 + HCl \xrightarrow[\text{sealed tube, 110°, 6 days}]{n\text{-pentane}} Me_2ClSnMn(CO)_5 \quad [49]\ I\text{-}18$$

$$Me_3SnMn(CO)_5 + \text{excess } HCl \xrightarrow[\text{sealed tube, 80°, 72 hours}]{n\text{-pentane}} MeCl_2SnMn(CO)_5 \quad [49]\ I\text{-}19$$

$$Ph_3SnRe(CO)_5 + \text{excess } HCl \xrightarrow[\text{-5 to -10°, 0.5 hours}]{CCl_4} Cl_3SnRe(CO)_5 \quad [50]\ 1\text{-}20$$

CHAPTER II

Cyclic Germoxy- and Stannoxy-carbene Complexes of Manganese and Rhenium

Introduction

As has been pointed out in Chapter I, both transition metal carbene complexes and transition metal-group IV metal complexes have been subjected to intensive study in recent years. However, prior to commencement of work in this group, only one report existed of a metal carbene complex with a group IV ligand other than carbon also present in the molecule. The complex *trans*-$Ph_3SnCo(CO)_3C(OEt)Ph$ and

$$Ph_3M'Co(CO)_4 + PhLi \rightarrow trans\text{-}Ph_3M'Co(CO)_3C(OLi)Ph \xrightarrow{Et_3OBF_4} trans\text{-}Ph_3M'Co(CO)_3C(OEt)Ph \qquad \text{II-1}$$

its lead analog were prepared by a conventional route (II-1).[51] The work presented in this thesis began as an attempt to prepare related derivatives of manganese and rhenium.

Work in this laboratory by Dr. W. K. Dean[52] has yielded a large number of derivatives notably of manganese, molybdenum and tungsten, in which both group IV and carbene ligands are present, though none of these have been of the

cyclic type described here. Typical syntheses are shown in II-2 and II-3. A crystal structure of *trans*-$(\eta\text{-}C_5H_5)$-$Mo(CO)_2(GePh_3)C(OEt)Ph$ has been completed.[53] This complex

$$(\eta\text{-}C_5H_5)M(CO)_3(M'Ph_3) + RLi \rightarrow trans\text{-}(\eta\text{-}C_5H_5)M(CO)_2(M'Ph_3)C(OLi)R \xrightarrow{R'_3O^+} trans\text{-}(\eta\text{-}C_5H_5)M(CO)_2(M'Ph_3)C(OR')R \quad [52]\ \text{II-2}$$

M = Mo, W; M' = Ge, Sn; R = Me, Ph, *t*-Bu; R' = Me, Et.

$$MeMn(CO)_5 + [Et_4N][GeCl_3] \rightarrow cis\text{-}[Cl_3GeMn(CO)_4C(O)Me][Et_4N] \xrightarrow{R_3O^+} cis\text{-}Cl_3GeMn(CO)_4C(OR)Me \quad [52]\ \text{II-3}$$

R = Me, Et.

shows structural features normally associated with metal carbene complexes. The molybdenum to carbene carbon distance of 2.06 Å is appreciably shorter than the Mo-C(sp^2) distance of 2.26 Å in $(\eta\text{-}C_5H_5)Mo(CO)_2(PPh_3)COMe$,[54] suggesting some degree of π interaction between the metal and carbene carbon atom. The carbene carbon to oxygen distance at 1.38 Å also suggests some degree of double bonding. The ethoxy group was found to be disordered but the point mid way between the two disordered positions of the oxygen atom lies on a plane defined by the carbene carbon and its other two substituent atoms. The plane of the phenyl ring is approximately perpendicular to the plane of the carbene

carbon and its three substituent atoms. These bonding features are similar to those described in Chapter I for $Cr(CO)_5C(OMe)Ph$, 4.[19] The formation of cyclic germoxy- and stannoxy-carbene complexes of the type described below from the intermediate acylate salts in II-2 is presumably precluded by the *trans* geometry. The reaction of the acylate salt in II-3 with $AgBF_4$, in an attempt to generate $Cl_2\overline{GeMn(CO)_4C(O)}Me$ or its dimer, yielded only $Cl_3GeMn(CO)_5$.[52]

In the following discussion of the formation of cyclic carbene derivatives, hydroxycarbene complexes are postulated as possible intermediates. In general such compounds are unstable and have been employed as intermediates to methoxy-carbene complexes which are formed upon reaction with diazo-methane[11] (I-1). However, some stable hydroxycarbene complexes have been isolated. With respect to the manganese sub-group, a stable hydroxycarbene complex of rhenium has been prepared, namely, $(\eta\text{-}C_5H_5)Re(CO)_2C(OH)Me$,[55] and stable manganese derivatives of the type *cis*-$XMn(CO)_4C(OH)Me$ have been prepared (X = Br, I).[56] In the manganese complexes stabilization occurs via hydrogen bonding between the hydroxy groups and halogen atoms.

The cyclic derivatives prepared in this work constitute only the second example of carbene complexes in which an element of group IV other than carbon is attached to the

carbene oxygen atom. The first example was the rather unstable, non-cyclic derivative $Cr(CO)_5C(OSiMe_3)Me$ prepared by Moser and Fischer.[57]

Synthesis and Characterisation of Complexes

The reaction of methyllithium with $Ph_3GeMn(CO)_5$ was found to proceed by attack at a carbonyl ligand *cis* to the group IV ligand to give the lithium acylate *cis*-$Ph_3GeMn(CO)_4C(OLi)Me$ (II-4). The acylate anion could be

$$Ph_3GeMn(CO)_5 + MeLi \xrightarrow{ether} cis\text{-}Ph_3GeMn(CO)_4C(OLi)Me \qquad \text{II-4}$$

$$cis\text{-}Ph_3GeMn(CO)_4C(OLi)Me + Et_4NBr \xrightarrow{water} [cis\text{-}Ph_3GeMn(CO)_4C(O)Me][Et_4N] + LiBr \qquad \text{II-5}$$

isolated as its pure, white tetraethylammonium salt by treating the lithium acylate with tetraethylammonium bromide in water (II-5). Treatment of the same lithium acylate with Et_3OBF_4 in water yielded the neutral carbene complex *cis*-$Ph_3GeMn(CO)_4C(OEt)Me$ (II-6). However, it was found

$$cis\text{-}Ph_3GeMn(CO)_4C(OLi)Me + Et_3OBF_4 \xrightarrow{water} cis\text{-}Ph_3GeMn(CO)_4C(OEt)Me \qquad \text{II-6}$$

unexpectedly that reaction of the lithium salt with either Me_3OPF_6 or $MeOSO_2F$ produced only a low yield of the expected *cis*-$Ph_3GeMn(CO)_4C(OMe)Me$ and predominantly a complex of

empirical formula $Ph_2GeMn(CO)_4COMe$ (II-7). The latter

$$cis\text{-}Ph_3GeMn(CO)_4C(OLi)Me + Me_3OPF_6 \text{ or } MeOSO_2F \xrightarrow{water} cis\text{-}Ph_3GeMn(CO)_4C(OMe)Me + Ph_2GeMn(CO)_4COMe \qquad II\text{-}7$$

could be prepared in a pure state as the sole carbonyl-containing product from treatment of the lithium salt with aqueous hydrochloric acid (II-8). The non-cyclic derivatives

$$cis\text{-}Ph_3GeMn(CO)_4C(OLi)Me + HCl \xrightarrow{water} Ph_2GeMn(CO)_4COMe + LiCl \qquad II\text{-}8$$

mentioned here will be discussed more fully in Chapter V, and the discussion in the present chapter will be confined largely to cyclic derivatives of which $Ph_2GeMn(CO)_4COMe$ was found to be an example.

Both cyclic and non-cyclic derivatives are prepared from lithium acylates of the type prepared in II-4. The geometry of these acylate salts is *cis* in all cases studied so far. This is fully consistent with the postulate of Darensbourg and Darensbourg which states that "when there is a choice of carbonyl groups within a molecule, nucleophilic attack always occurs at the CO group with the greater stretching force constant."[51] A greater stretching force constant implies a lower electron density at carbon. In mono-substituted manganese- and rhenium-pentacarbonyl

complexes the *cis* carbonyl groups always have a higher stretching force constant than the *trans*[8] (see Chapter VII), and thus methyllithium attack would be expected to occur at a carbonyl group *cis* to the group IV ligand, as is observed.

By a route analogous to II-8 products of empirical formulae $Me_2GeMn(CO)_4COMe$, $Ph_2GeRe(CO)_4COMe$, $Me_2GeRe(CO)_4COMe$ and $Me_2SnRe(CO)_4COMe$ have been prepared. The structures of these complexes have been established through the use of analyses, mass spectrometry, infrared spectroscopy, and ^1H and ^{13}C NMR spectroscopy as described below. All compounds are white when pure and in the solid state the rhenium derivatives are quite air-stable. The diphenylgermyl-manganese derivative is mildly air-sensitive, decomposing over *ca.* 24 hours, and $Me_2GeMn(CO)_4COMe$ becomes yellow after exposure to air for 1 hour.

All five complexes of this type were found to have four carbonyl stretching bands in solution infrared spectra, indicative of *cis*-disubstituted geometries at the central metal atom (see Figures 1-5 and Table I). The rhenium complexes are neither very soluble nor very stable in hydrocarbon solvents and their spectra were recorded in dichloromethane in which $Me_2GeRe(CO)_4COMe$ and $Me_2SnRe(CO)_4COMe$ are quite stable. However, $Ph_2GeRe(CO)_4COMe$ is not at all stable in solution and even in dichloromethane its infrared spectrum must be recorded quickly before peaks due to decomposition products begin to appear. Also, for this

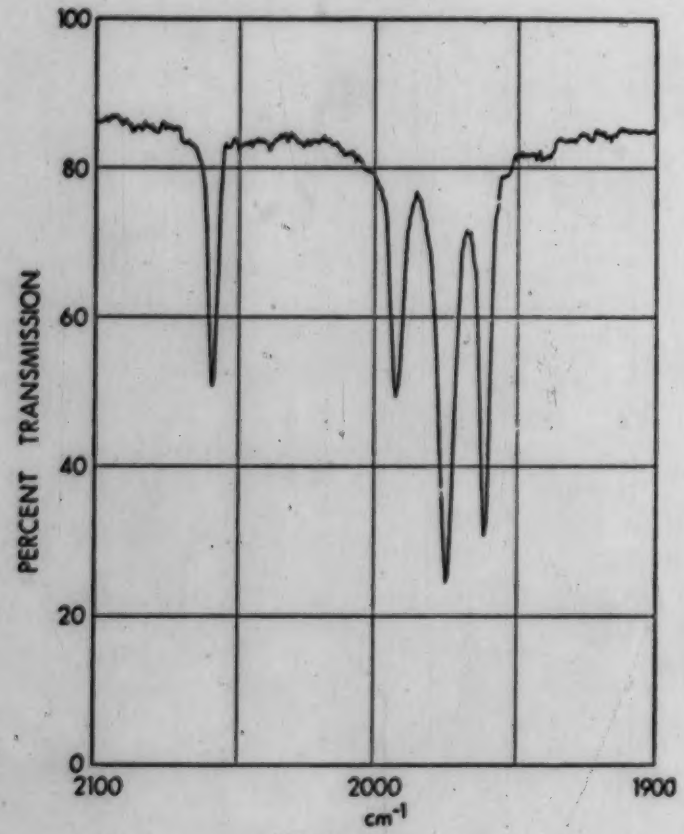


Figure 1

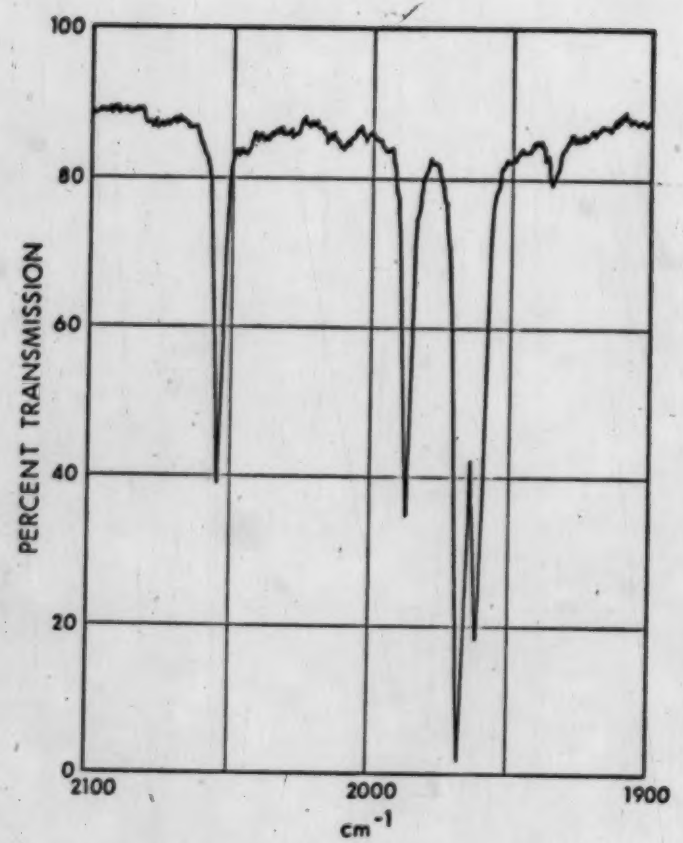


Figure 2

Figure 1. Infrared spectrum [ν(CO) region] of $Ph_2GeMn(CO)_4COMe$ in *cyclo*hexane.

Figure 2. Infrared spectrum [ν(CO) region] of $Me_2GeMn(CO)_4COMe$ in *cyclo*hexane.

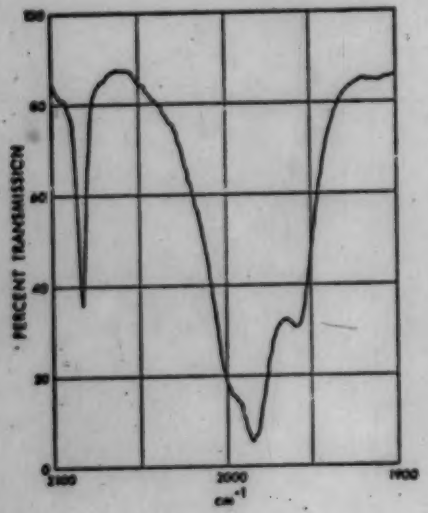


Figure 3

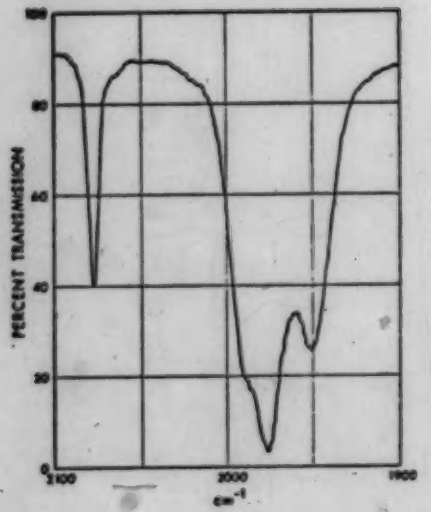


Figure 4

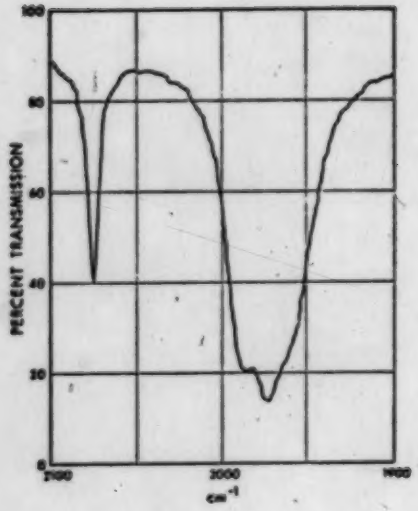


Figure 5

Figure 3. Infrared spectrum [ν(CO) region] of $Ph_2GeRe(CO)_4COMe$ in CH_2Cl_2.

Figure 4. Infrared spectrum [ν(CO) region] of $Me_2GeRe(CO)_4COMe$ in CH_2Cl_2.

Figure 5. Infrared spectrum [ν(CO) region] of $Me_2SnRe(CO)_4COMe$ in CH_2Cl_2.

TABLE I

CARBONYL STRETCHING FREQUENCIES, AND MASS SPECTRAL PARENT IONS FOR THE CYCLIC CARBENE DERIVATIVES OF MANGANESE AND RHENIUM

Empirical Formula	Mass Spectral Parent Ion (m/e)[a]	Carbonyl Stretching Frequencies (cm^{-1})[c,d]
$Ph_2GeMn(CO)_4COMe$	438	2059 (m), 1992 (m), 1975 (vs), 1962 (s)
$Me_2GeMn(CO)_4COMe$	314	2054 (m), 1986 (m), 1966 (vs), 1960 (s)
$Ph_2GeRe(CO)_4COMe$	568	2083 (m), 1994 (s,sh), 1983 (vs), 1957 (m)
$Me_2GeRe(CO)_4COMe$	444[b]	2077 (m), 1987 (s,sh), 1975 (vs), 1948 (s)
$Me_2SnRe(CO)_4COMe$	490	2075 (m), 1986 (s,sh), 1973 (vs), 1961 (s,sh)

[a]Most abundant peak of isotope combination pattern of parent ion reported; isotope combination pattern of parent ion agrees with computer simulated pattern in all cases.

[b]Parent ion due to monomer observed even though sample used known to be dimeric by X-ray crystallography.

[c]*Cyclo*hexane solvent for manganese complexes, dichloromethane for rhenium derivatives.

[d]m = medium, s = strong, v = very, sh = shoulder.

reason, a satisfactory ^1H NMR spectrum of this complex has not been obtained. Decomposition occurs rapidly in the NMR sample tube whether the solution is made up in air, or under vacuum using carefully degassed solvent, but ^1H NMR spectra in CD_2Cl_2 indicate that the decomposition products are different in the two cases. The two manganese complexes are more stable in *cyclo*hexane solutions than are their rhenium analogs but are observed to decompose if solutions are left in the infrared cells. Infrared spectra indicate that $Ph_2GeMn(CO)_4COMe$ decomposes in *cyclo*hexane to $MeCOMn(CO)_5$ and hence to $MeMn(CO)_5$ over the course of several days.

All five complexes of this type show parent ions in the mass spectrometer corresponding to monomeric units. Figure 6 shows the computer simulated isotope combination pattern for the parent ion of $Me_2SnRe(CO)_4COMe$ to which the observed pattern was in very close agreement. However, ^1H NMR studies have shown that dimer-monomer equilibria exist in solutions of $Me_2GeMn(CO)_4COMe$ and $Me_2GeRe(CO)_4COMe$, while osmometric-molecular weight determinations indicate that in dilute solutions $Me_2GeMn(CO)_4COMe$ exists largely as monomeric units while $Me_2SnRe(CO)_4COMe$ is predominantly dimeric (see Chapter III for details of the dimer-monomer equilibria). The ^1H NMR data fully support the suggested empirical formulae of the new complexes and further confirmation comes from analytical data (see Tables II and III).

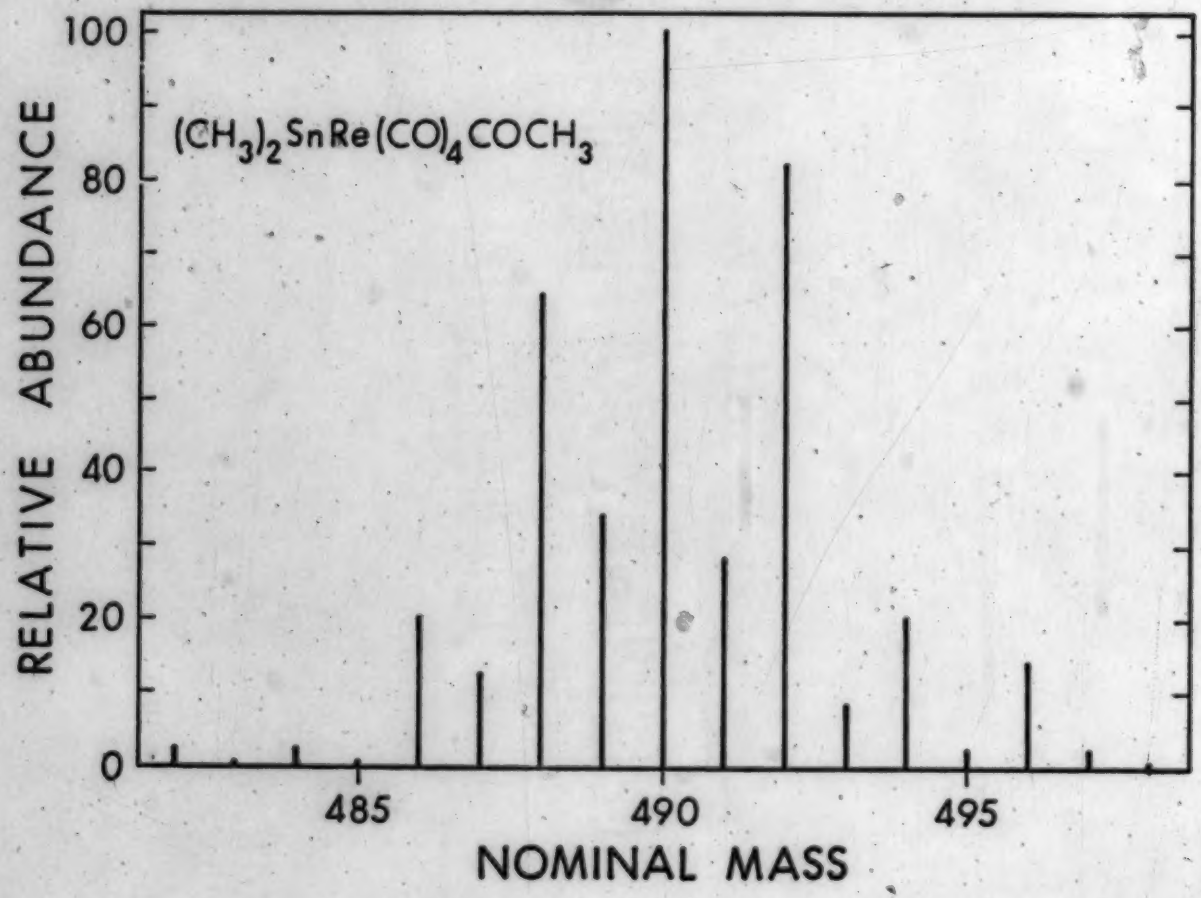


Figure 6. Calculated mass spectral isotope combination pattern for the parent ion of $Me_2SnRe(CO)_4COMe$.

TABLE II

^{1}H NMR DATA FOR THE CYCLIC CARBENE DERIVATIVES OF MANGANESE AND RHENIUM

Empirical Formula	Chemical Shift (τ-value)[a] C-CH$_3$	Ge-(CH$_3$)$_2$ or Sn-(CH$_3$)$_2$	Solvent
$Ph_2GeMn(CO)_4COMe$[b]	7.19	—	CD_2Cl_2
$Me_2GeMn(CO)_4COMe$	7.32[c]	8.90	CD_2Cl_2
$Ph_2GeRe(CO)_4COMe$	Satisfactory spectrum not obtained--see text		
$Me_2GeRe(CO)_4COMe$	7.23[d], 7.35[c]	8.93	CD_2Cl_2
$Me_2SnRe(CO)_4COMe$	7.32[d,e]	9.16[f]	CD_2Cl_2

[a]Relative to TMS at 10 τ. Peak integrals consistent with empirical formulae.

[b]Ph resonance complex multiplet with most intense peak at τ 2.53.

[c]Due to monomeric species.

[d]Due to dimeric species.

[e]$^4J(^{117}, ^{119}Sn-^1H) = 6$ Hz.

[f]$^2J(^{117}, ^{119}Sn-^1H) = 31$ Hz.

TABLE III

ANALYTICAL DATA, MELTING POINTS, AND YIELDS FOR THE CYCLIC CARBENE DERIVATIVES OF MANGANESE AND RHENIUM

Empirical Formula[a]	% Yield[b]	M.P. (°C)	Calcd. % C	Calcd. % H	Found %[c] C	Found %[c] H
$Ph_2GeMn(CO)_4COMe$[d]	88	127-8	49.49	3.00	49.51	3.17
$Me_2GeMn(CO)_4COMe$	87	86-7	30.73	2.90	29.97	3.00
$Ph_2GeRe(CO)_4COMe$	83	149-52 dec.	38.06	2.31	37.17	2.31
$Me_2GeRe(CO)_4COMe$	83	135-7[f]	21.64	2.04	21.81	2.21
$Me_2SnRe(CO)_4COMe$[e]	62	dec. > 165	19.61	1.85	19.61	1.82

[a]All complexes white in colour when pure.

[b]Yields represent amount of crude product precipitated from aqueous solution and found to be analytically pure, except in the case of $Me_2SnRe(CO)_4COMe$ for which all data apply to recrystallized material.

TABLE III (continued)

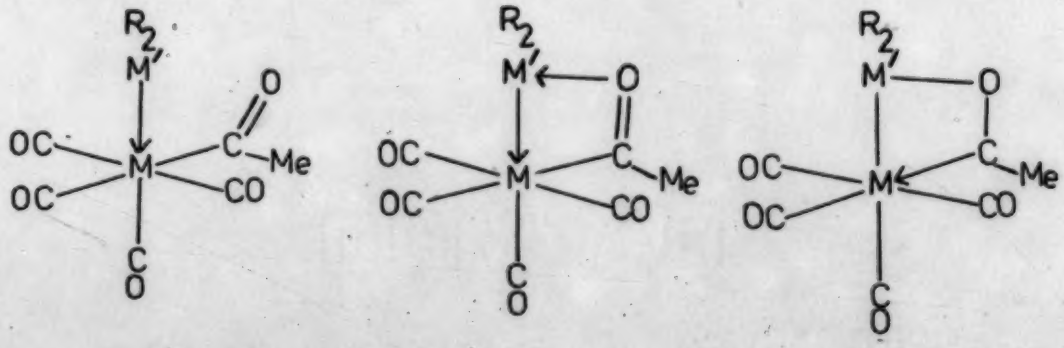
[c]C,H analyses carried out in duplicate by the Microanalytical Laboratory of this Department (mean value given), except for $Me_2SnRe(CO)_4COMe$ for which a single determination was carried out by Alfred Bernhardt, Microanalytisches Laboratorium, West Germany.

[d]Calcd.: C = 49.49; H = 3.00; Mn = 12.58; Ge = 16.62. Found: C = 49.25; H = 3.27; Mn = 12.11; Ge = 16.47. (Single determinations, Alfred Bernhardt).

[e]Calcd.: Sn = 24.22; O = 16.32. Found: Sn = 24.10; O = 16.19. (Single determinations, Alfred Bernhardt).

[f]Sample used for M.P. determination known to be dimeric by X-ray crystallography.

On the basis of the above evidence several alternative formulations could be considered for these compounds. If we consider just the monomeric species, and accept that similar structural alternatives can exist for the dimeric forms, structures 15, 16 and 17 may be discussed. As infra-red bands in solid state (KBr disc and Nujol) spectra of



15 16 17

these complexes did not appear around 1600 cm^{-1}, as required for a free acetyl group, structure 15 which would constitute a true germylene or stannylene complex can be eliminated, and we need consider only 16 and 17 in which the oxygen atom is interacting with the group IV metal. Structure 16 contains a coordinated acetyl oxygen atom and a carbon atom which would presumably retain appreciable acetyl character and 16 is thus related to the derivatives prepared by Marks *et al.*[29,30] described in Chapter I. In 17 a carbene carbon atom is present. Through the use of ^{13}C NMR spectroscopy it has been possible to show that the carbon atom in question has essentially carbene character.

The peak due to the carbene carbon atom of the monomeric form of $Me_2GeMn(CO)_4COMe$, which we can now represent as $Me_2\overline{GeMn(CO)_4C(O)}Me$, is observed at -338.0 p.p.m. relative to TMS in a $CDCl_3$ solution at ambient temperature. This is in good agreement with the highly deshielded carbene chemical shifts previously observed. For example, the first-row complex $Cr(CO)_5C(OEt)Me$ exhibits a carbene carbon resonance at -357.3 p.p.m.[21] Furthermore, the dimeric form of $Me_2GeRe(CO)_4COMe$ gives a ^{13}C NMR peak at -305.7 p.p.m. in close agreement with the carbene carbon resonance of the novel complex *cis*-$Me_3GeRe(CO)_4C(OEt)Me$ (see Chapter V) which occurs at -314.8 p.p.m. This region is well removed from that in which one finds acyl carbon resonances of metal acyls. For example, in $MeCORe(CO)_5$ and $PhCORe(CO)_5$ acyl carbon resonances occur at -244.0 and -245.4 p.p.m. (see Chapter VII). Fuller details of ^{13}C NMR results for new carbene derivatives are discussed in Chapter VI.

The differentiation between structures 16 and 17 is not as clear-cut as might appear from the diagrams. Complexes related to 16 as prepared by Marks[29] have been shown to possess the group IV atom in the +4 oxidation state,[32] not the +2 state as a diagram of the type 16 might suggest. Thus, 16 and 17 are quite closely related. Indeed they may be viewed as potential canonical forms representing the actual structure. However, the ^{13}C NMR results show that the molecules possess carbon atoms with a high degree of

carbene character and we therefore refer to such derivatives as cyclic germoxy- and stannoxy-carbene complexes of manganese and rhenium.

The cyclic nature of the complexes has been further confirmed by X-ray structural work carried out by Drs. L. Y. Y. Chan and M. J. Bennett of this Department. Recrystallization of a crude sample of $Me_2GeRe(CO)_4COMe$ yielded excellent crystals which have been shown by X-ray crystallography to contain the dimeric form of the complex (Figure 7). Bond lengths and angles for $[Me_2GeRe(CO)_4COMe]_2$ are given in Table IV. A list of fractional atomic coordinates can be found in Appendix I.

The molecule contains an unusual eight-membered heterocyclic ring of rhenium, germanium, oxygen and carbon atoms. This structure is consistent with the cyclic germoxy-carbene formulation we have suggested on the basis of ^{13}C NMR, but does not unambiguously distinguish between a carbene of the type 17 and a complex containing a coordinated acetyl group akin to 16. Both carbene and acetyl carbon atoms would be expected to have planar enviroments as observed. The germanium-oxygen distance at 1.96 Å is significantly longer than in an iron-digermoxane complex $[(\eta\text{-}C_5H_5)(CO)_2FeGeMe_2]_2O$ where a value of 1.785 Å was obtained.[58] The significant lengthening of the germanium oxygen bond in $[Me_2GeRe(CO)_4COMe]_2$ could clearly be consistent with a coordinated acetyl

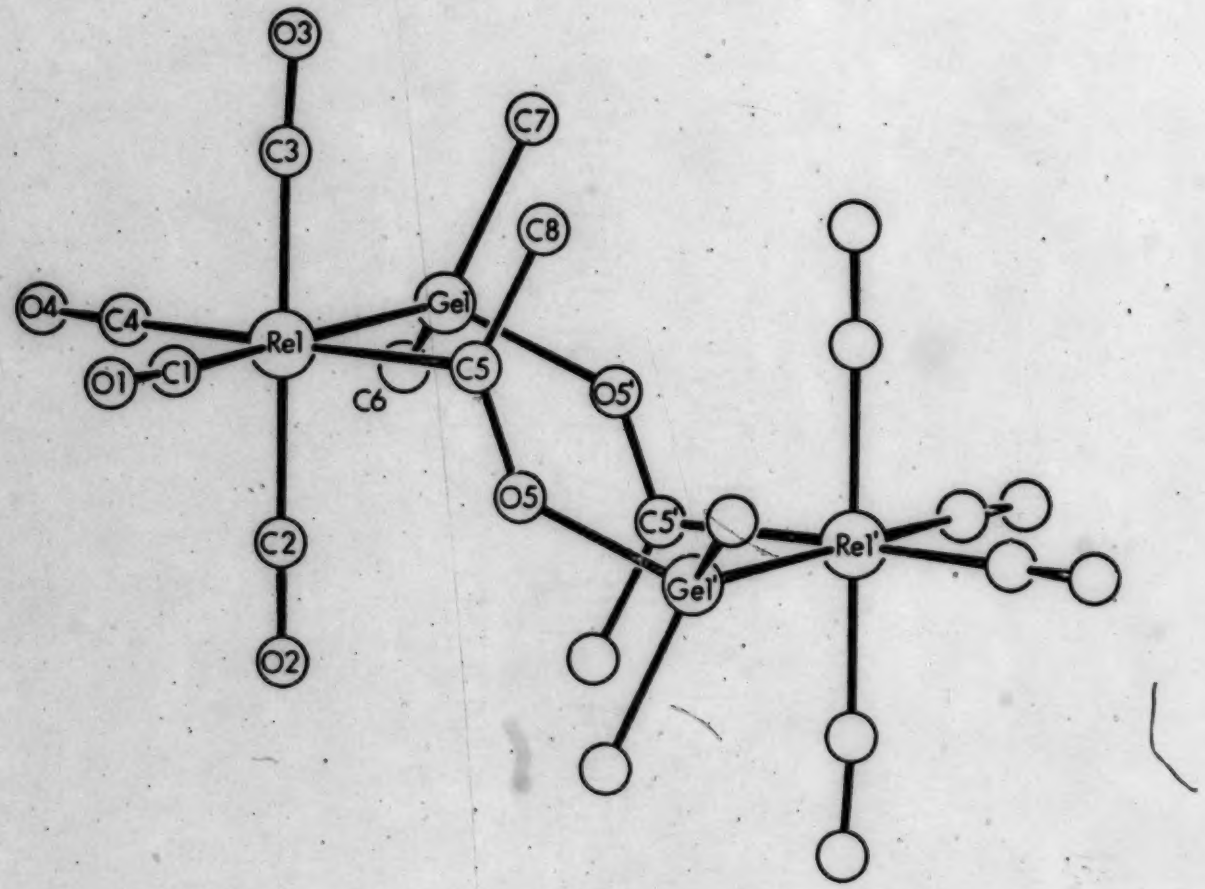


Figure 7. Molecular structure of $[Me_2GeRe(CO)_4COMe]_2$.

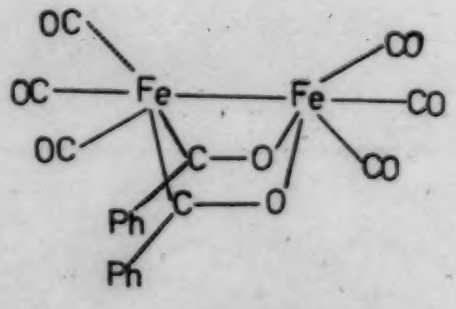
TABLE IV

INTRAMOLECULAR DISTANCES AND ANGLES FOR $[Me_2GeRe(CO)_4COMe]_2$

Distance	Å	Angle	Degrees
Re1-Ge1	2.591 (3)	Ge1-Re1-C1	173.3 (7)
Re1-C1	1.90 (3)	Ge1-Re1-C2	90.7 (6)
Re1-C2	1.98 (2)	Ge1-Re1-C3	86.1 (9)
Re1-C3	1.86 (3)	Ge1-Re1-C4	91.3 (9)
Re1-C4	1.97 (3)	Ge1-Re1-C5	82.8 (9)
Re1-C5	2.14 (3)	C1-Re1-C2	92.9 (9)
Ge1-O5'	1.96 (2)	C1-Re1-C3	90.5 (1.1)
Ge1-C6	1.97 (3)	C1-Re1-C4	94.5 (1.3)
Ge1-C7	2.00 (3)	C1-Re1-C5	91.7 (1.3)
C1-O1	1.17 (3)	C2-Re1-C3	176.3 (1.0)
C2-O2	1.17 (3)	C2-Re1-C4	89.3 (1.4)
C3-O3	1.20 (3)	C2-Re1-C5	87.1 (1.3)
C4-O4	1.08 (3)	C3-Re1-C4	88.9 (1.4)
C5-O5	1.27 (3)	C3-Re1-C5	94.3 (1.4)
C5-C8	1.56 (4)	C4-Re1-C5	173.0 (8)
		C6-Ge1-C7	106.9 (1.6)
		C6-Ge1-Re1	123.0 (9)
		C7-Ge1-Re1	118.4 (9)
		O5'-Ge1-Re1	107.6 (9)
		O5'-Ge1-C6	102.8 (1.0)
		O5'-Ge1-C7	92.4 (9)
		Re1-C5-O5	120.6 (1.6)
		Re1-C5-C8	110.8 (1.8)
		O5-C5-C8	127.7 (2.0)
		Ge1-O5'-C5'	139.3 (1.4)
		Re1-C1-O1	175.2 (2.1)
		Re1-C2-O2	176.2 (1.6)
		Re1-C3-O3	177.6 (2.4)
		Re1-C4-O4	174.9 (2.5)

structure akin to 16, but it could also be consistent with a cyclic carbene structure if one accepts that a strong interaction between oxygen and an electronegative carbene carbon atom might well reduce the normal degree of double bonding between oxygen and germanium, thus lengthening the latter bond. This is, of course, speculative and an example of a suitable structure for comparison purposes does not exist in the literature. In this regard it may well be worthwhile to carry out the crystal structure of a germanium acetate complex to see if a similar germanium-oxygen bond lengthening occurs, since an acetyl group might be expected to have a similar electron-withdrawing effect on the germanium-oxygen bond.

The carbon-oxygen bond length C5-O5 at 1.27(3) Å also does not distinguish unambiguously between carbene and coordinated acetyl type structures. This value is close to



18

that observed for the complex 18 at 1.26(1) Å. In a paper discussing the structure of 18,[59] it was clearly explained that such a bond length is intermediate between those expected for acetyl and carbene groups and that no distinction could therefore be made on this basis. Unfortunately X-ray crystal structures of other rhenium carbene complexes which might be useful for comparison purposes are not available. Thus, from the above discussion it can be seen that X-ray crystallography has confirmed the formulation of the new complexes as heterocycles, but that the evidence suggesting that they contain carbene carbon atoms has come primarily from ^{13}C NMR.

At present it is not known whether the cyclic derivatives exist in their monomeric or dimeric forms when precipitated from water in their crude states. The sharp melting points of compounds of empirical formulae $Ph_2GeMn(CO)_4COMe$, $Me_2GeMn(CO)_4COMe$ and $Ph_2GeRe(CO)_4COMe$ in their crude states imply that only one form is present. Mass spectra of the complexes are not helpful as peaks due to only the monomeric species are observed in all cases, even in the case of a recrystallized sample of $Me_2GeRe(CO)_4$-COMe which is known to be dimeric by X-ray crystallography.

To complete the discussion of the cyclic derivatives prepared to date, a few other features of their spectroscopic properties can be mentioned. As noted earlier all five complexes show parent ions in the mass spectrometer

corresponding to monomeric units. The spectrum of $Ph_2GeMn(CO)_4COMe$ shows competing losses of methyl and carbonyl groups from the parent ion and also exhibits a very intense peak at m/e 243 assigned to the Ph_2MeGe^+ ion presumably arising from methyl migration. The spectrum of $Me_2GeMn(CO)_4$-COMe shows similar features including a peak due to Me_3Ge^+ at m/e 119; the spectrum in this case was recorded at a source temperature of only 30°, a temperature at which this complex is known to be stable, and this suggests that the observed peak arises as a result of electron impact rather than thermal decomposition of the complex. For the complexes $Ph_2GeRe(CO)_4COMe$, $Me_2GeRe(CO)_4COMe$ and $Me_2SnRe(CO)_4COMe$ loss of a methyl group from the parent ion appears to be favoured over carbonyl loss and the phenomenon of a methyl group migration onto the group IV atom is much less pronounced.

In the ^1H NMR spectrum of $Me_2SnRe(CO)_4COMe$ (Figure 8) the tin to methyl-hydrogen two-bond coupling constant was found to be 31 Hz. The significance of this is difficult to interpret at present. For derivatives of the type $Me_3SnM(CO)_5$ (M = Mn, Re) corresponding values are ~ 45-50 Hz.[60] Grossly different values for two closely related derivatives prepared by Marks *et al.* have been observed, namely, 41.2 Hz for $(py)Me_2SnFe(CO)_4$[30] (py = pyridine) and 23.0 Hz for $(THF)Me_2SnCr(CO)_5$.[29] At the present time insufficient data exists for an attempt to be made to

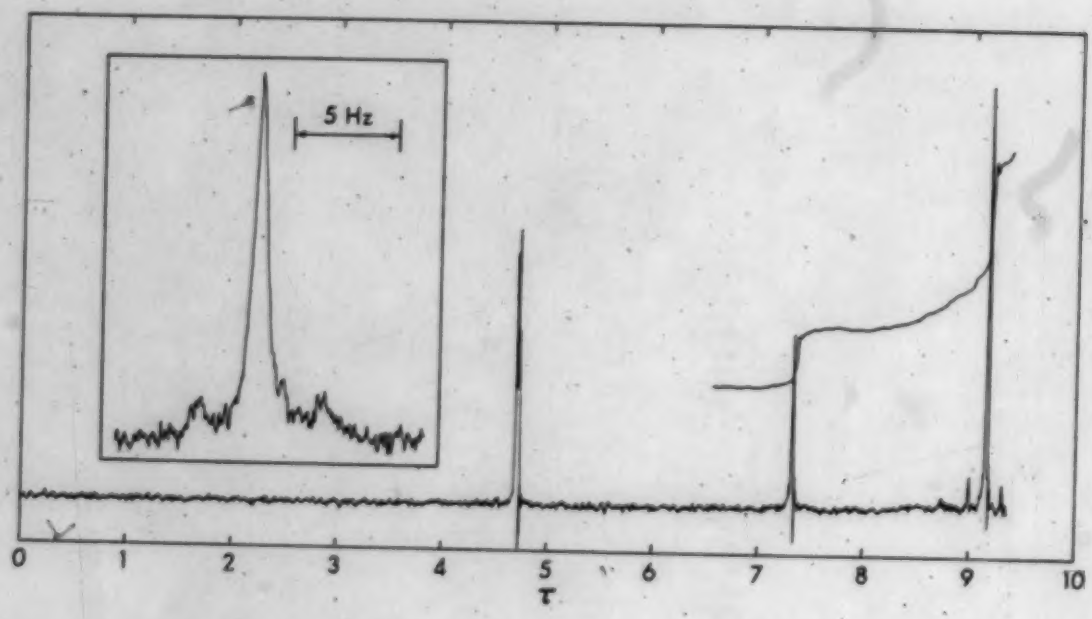


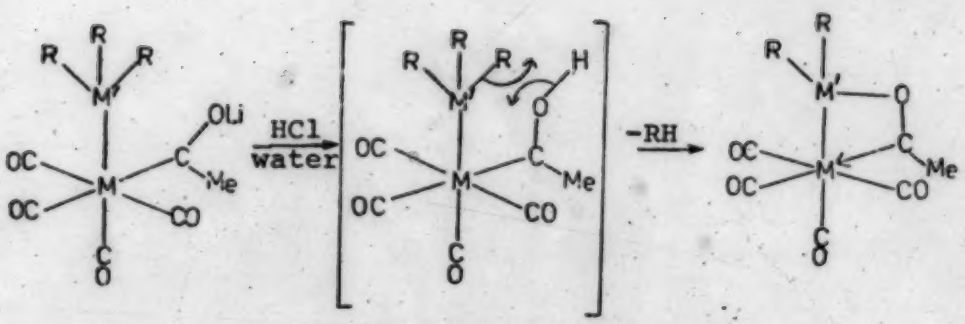
Figure 8. ^{1}H NMR spectrum of $[Me_2SnRe(CO)_4COMe]_2$ in CD_2Cl_2 (including an expansion of the C-C$\underline{H}_3$ region).

distinguish between structural possibilities such as 16 and 17 on the basis of the observed coupling constant for $[Me_2SnRe(CO)_4COMe]_2$. The four-bond coupling of tin to the carbene methyl-hydrogens was observed at 6 Hz and could correspond to coupling across either rhenium or oxygen. A value of 13 Hz was observed for the four-bond coupling across manganese in *cis*-$Ph_3SnMn(CO)_4C(OEt)Me$ (see Chapter V).

Possible Reaction Mechanisms

As described above, it has been established that the reaction of lithium salts of the type *cis*-$R_3M'M(CO)_4C(OLi)Me$ with aqueous hydrochloric acid yields precipitates of novel cyclic carbene complexes (II-8). The mechanism by which an organic group is cleaved from the group IV metal has not been ascertained but likely possibilities can be postulated. One is that acid cleavage of the organic group occurs directly, promoted, accompanied or followed by coordination to the group IV atom of an oxygen atom, rather than a chloride ion as in I-17-20.

Another possibility is that a reactive hydroxycarbene intermediate, 19, is formed and then cyclises in a four-centre type of process (II-9). This appears feasible since it is known that lithium acylates are readily protonated to give hydroxycarbene complexes.[11] If the intermediate 19 is involved it is of course quite possible that two such



II-9

19

R = Ph, Me; M = Mn; M' = Ge. R = Me; M = Re; M' = Ge, Sn. R = Ph; M = Re; M' = Ge.

molecules could combine to eliminate two molecules of RH giving either one molecule of dimer or two molecules of monomer.

In cases where R = Me the protonation reaction was accompanied by vigorous gas evolution, presumably due to the formation of methane. The reaction of *cis*-$Ph_3GeMn(CO)_4$-C(OLi)Me with Me_3OPF_6 in water (II-7) results largely in the formation of cyclic product. A G.L.C. analysis of the organic product of this reaction revealed it to be benzene (no toluene was present), and thus the cyclic product must result from protonation of the lithium acylate in this reaction.

Some Unsuccessful Reactions

Attempts have been made to form related cyclic derivatives in an effort to extend the work described above. Some of these reactions will now be described. The reaction of $Ph_3PbMn(CO)_5$ with MeLi in ether appeared to yield a lithium acylate by infrared spectroscopy in a reaction analogous to II-4. However, this intermediate appeared to be unstable in water and the yellow aqueous solution rapidly turned brown. No attempt was made to protonate the intermediate, but attempted ethylation with Et_3OBF_4 yielded only a black precipitate. An infrared spectrum of this material in a hydrocarbon solution showed the presence of a little $Ph_3PbMn(CO)_5$ but no other carbonyl-containing species.

Protonation of *cis*-$Ph_3SnMn(CO)_4C(OLi)Me$ with aqueous hydrochloric acid produced an orange tar which solidified when dried under vacuum. This material was very unstable in *cyclo*hexane solution and has not been characterised. The reaction of the analogous trimethyltin-salt yields a yellow-brown oil which solidifies upon stirring in the aqueous solution. After drying, an infrared spectrum in methylene chloride solution reveals a complex mixture of products.

Infrared spectra have indicated that $Me_3SiMn(CO)_5$ reacts with methyllithium to give the expected lithium

acylate, analogous to II-4, but protonation with aqueous hydrochloric acid induces metal-metal bond cleavage, yielding $Mn_2(CO)_{10}$ as the carbonyl-containing product.

The reaction of *trans*-$Ph_3GeW(CO)_4NO$[61] with MeLi in ether appeared to give an anionic complex by infrared spectroscopy. Attempts at ethylation and protonation resulted in much decomposition and the small amounts of carbonyl-containing products obtained have not been characterised.

It has also been found that $(\eta\text{-}C_5H_5)Fe(CO)_2SiPh_3$ and $(\eta\text{-}C_5H_5)Fe(CO)_2SiMe_2Ph$ do not react with MeLi in ether, and the latter complex simply decomposes slowly in the presence of *t*-BuLi without apparent formation of a new carbonyl derivative.

EXPERIMENTAL

All reactions were carried out at ambient temperature under a static nitrogen atmosphere and solid products were handled with minimum exposure to air. Ether and tetrahydrofuran were dried by distillation from calcium hydride and solvents were saturated with nitrogen prior to use. Published procedures were used for the preparation of $Me_3GeMn(CO)_5$,[62] $Ph_3GeMn(CO)_5$,[63] $Ph_3GeRe(CO)_5$,[64] and $Me_3SnRe(CO)_5$,[60] employing the general method as outlined by Gorsich[48] in all cases. We believe that $Me_3GeRe(CO)_5$ is a new compound and its preparation by the same general method is described below.

Dirhenium decacarbonyl was purchased from the Pressure Chemical Co., Pittsburgh and dimanganese decacarbonyl from Strem Chemicals Inc., Danvers, Mass. Trimethyltin- and triphenyltin-chloride were obtained from M & T Chemicals Inc., Richmond, Ca.; triphenylgermanium chloride from Strem Chemicals Inc.; and trimethylgermanium bromide from Alfa Inorganics Inc., Beverly, Mass. Solutions of methyllithium in ether were also obtained from Alfa Inorganics Inc.

Melting points were determined using a Kofler hot stage apparatus. Solution infrared spectra were recorded using a Perkin-Elmer Model 337 grating spectrophotometer with scale expansion and were calibrated using gaseous CO.[60] Solid state (KBr disc) infrared spectra were

supplied by the spectroscopy laboratory of this Department and recorded using a Perkin-Elmer 421 spectrometer.

Microanalyses were performed by the microanalytical laboratory of this Department and by the Alfred Bernhardt Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, Fritz-Pregl-Strasse 14-16, West Germany.

Natural abundance ^{13}C NMR spectra were obtained using the Fourier transform pulsed NMR technique with proton decoupling. Varian HA 100 and Bruker HFX-90 spectrometers were used, operating at 25.15 MHz and 22.6 MHz respectively. ^{1}H NMR spectra were recorded using Varian A60, A56/60, or HA 100 instruments.

Mass spectra were obtained by electron impact (70eV), employing a direct probe, using Associated Electronics Industries MS-2, MS-9 or MS-12 instruments.

The gas chromatographic analysis was carried out using an Aerograph Manual Temperature Programmer Gas Chromatograph (Model A-90-P) using helium as carrier gas.

Preparation of $Me_3GeRe(CO)_5$

The method of Gorsich[48] was used. Dirhenium decacarbonyl (5.0 g, 7.7 mmol) was reduced to $(OC)_5Re^-Na^+$ by the action of sodium amalgam in tetrahydrofuran. Trimethylgermanium bromide (4.0 g, 20.2 mmol) was added and stirring continued for two hours. Removal of solvent on a rotary

evaporator, followed by recrystallization from acetone/water yielded the white product (2.53 g, 41%) [M.P. 58-9°C; IR(*cyclo*hexane) ν(CO) 2111 (w), 2002 (vs), 1995 (m); Mass spec. parent m/e 444; ^{1}H NMR ($CDCl_3$) singlet τ 9.41. Analysis, calcd. (%): C, 21.64; H, 2.04. Found (%): C, 21.56; H, 1.67].

Preparation of Cyclic Carbene Complexes

To $Me_3GeMn(CO)_5$ (5.0 g, 16.0 mmol) dissolved in *ca.* 100 ml dry ether was added from a syringe an ethereal solution of 1.5 M MeLi (11.0 ml, 16.5 mmol). A rapid colour change from colourless to yellow was observed. After a few minutes the solution infrared spectrum taken in ether indicated the total disappearance of starting material and formation of *cis*-$Me_3GeMn(CO)_4C(OLi)Me$. The ether solvent was removed under vacuum to leave a yellow-brown, oily residue. This was extracted with *ca.* 60 ml water, filtered and dilute hydrochloric acid was then added dropwise to the clear, yellow solution. Initially some turbidity was observed and vigorous gas evolution accompanied the formation of a yellow oil which floated to the top of the aqueous solution. This oil solidified when gas evolution ceased to give a pale yellow material. (The pH after completion of the acid addition was approximately 2, as shown by pHydrion papers). The product was filtered, washed with 2 x 20 ml water and dried under vacuum. The above

method was used to synthesize $Me_2SnRe(CO)_4COMe$, $Me_2GeRe(CO)_4$-COMe, $Ph_2GeMn(CO)_4COMe$ and $Ph_2GeRe(CO)_4COMe$, though usually on smaller scales. In the latter two cases gas evolution was not observed during addition of the acid.

Yields were good and the products were analytically and spectroscopically pure except in the case of $Me_2SnRe(CO)_4COMe$. This complex was purified by dissolving in dichloromethane and adding *n*-heptane, removing dichloromethane under reduced pressure to the point of turbidity, and cooling the solution to -15°C. The same method was used to obtain crystals of $Me_2GeRe(CO)_4COMe$ (actually in its dimeric form) suitable for X-ray crystallography. For the complexes which were analytically pure without recrystallization, the crude solids were either white or pale yellow, the yellow colour presumably arising from adsorbed traces of impurities which did not show up spectroscopically. The data presented in Tables I-III applies to the crude solids except as noted.

Gas Chromatographic Work

Treatment of *cis*-$Ph_3GeMn(CO)_4C(OLi)Me$ with Me_3OPF_6 as described in Chapter V yields a solid mixture of the cyclic $Ph_2GeMn(CO)_4COMe$ and *cis*-$Ph_3GeMn(CO)_4C(OMe)Me$. The solid was removed by filtration and the aqueous filtrate extracted with 2 x 5 ml *n*-pentane. The pentane extracts were combined

and dried over anhydrous sodium sulphate. The solution volume was then reduced to a few drops by rotary evaporation.

Benzene and toluene as *n*-pentane solutions were separately introduced into the gas chromatograph to establish their retention times. The *n*-pentane solution from above was then introduced and was found to contain benzene and not toluene. To ensure that the *n*-pentane solvent employed did not contain benzene a 10 ml sample was reduced in volume to a few drops and a portion injected into the gas chromatograph; no benzene was present. Finally the retention times of the benzene and toluene standards were rechecked and were found to be unchanged during the course of the experiment.

CHAPTER III

Dimer-Monomer Equilibria in Solutions of Cyclic Germoxy- and Stannoxy-carbene Complexes of Manganese and Rhenium

Introduction

In Chapter II a number of novel heterocyclic carbene derivatives have been described. The empirical formulae of the complexes were established by analytical data, and mass and infrared spectra were consistent with monomeric formulations for the complexes. However, variable temperature and variable concentration ^{1}H NMR studies have since established that dimer-monomer equilibria exist in solutions of $Me_2GeMn(CO)_4COMe$ and its rhenium analog. In the former case ^{13}C NMR has been used to indicate that both monomeric and dimeric species contain carbene carbon atoms (see Chapter VI). The existence of a dimeric form for $Me_2GeRe(CO)_4COMe$ has also been established by X-ray crystallography (see Chapter II). The type of dimer-monomer equilibrium described here is without precedent in the field of metal carbene chemistry, and earlier variable temperature ^{1}H NMR studies have involved only intramolecular phenomena, namely, restricted rotations about metal to carbene carbon bonds[65] or about carbene carbon to heteroatom bonds.[66]

Results and Discussion

The ^1H NMR of $Me_2GeMn(CO)_4COMe$ at 31°C in CD_2Cl_2 clearly shows the resonances expected for the methyl group attached to the carbene carbon and the two methyl groups attached to germanium at τ 7.32 and τ 8.90 respectively (see Figure 9). A rather concentrated solution was used to obtain this spectrum and there was some evidence that a peak of low intensity exists to slightly lower field than the C-$C\underline{H}_3$ resonance. The solution was therefore cooled and Figure 9 shows that at low temperatures two pairs of peaks are clearly visible. This process was found to be completely reversible. A low temperature ^{13}C NMR spectrum in $CDCl_3$ exhibits peaks at -337.6 and -335.1 p.p.m. indicating that both species present contain carbene carbon atoms. The ^{13}C NMR of the dimeric form of $Me_2GeRe(CO)_4COMe$ also favours a metal carbene formulation (see Chapter VI for a further discussion of ^{13}C NMR spectra). On the basis of these results a quantitative ^1H NMR study was undertaken to determine the nature of the low temperature species. The two peaks due to the C-$C\underline{H}_3$ groups of the monomer and dimer near τ 7.32 were reasonably well separated (17.5 Hz) and their relative intensity could be determined through the use of peak integrals. Both variable temperature and variable concentration studies have been carried out and the latter have proved crucial in establishing the nature of this phenomenon.

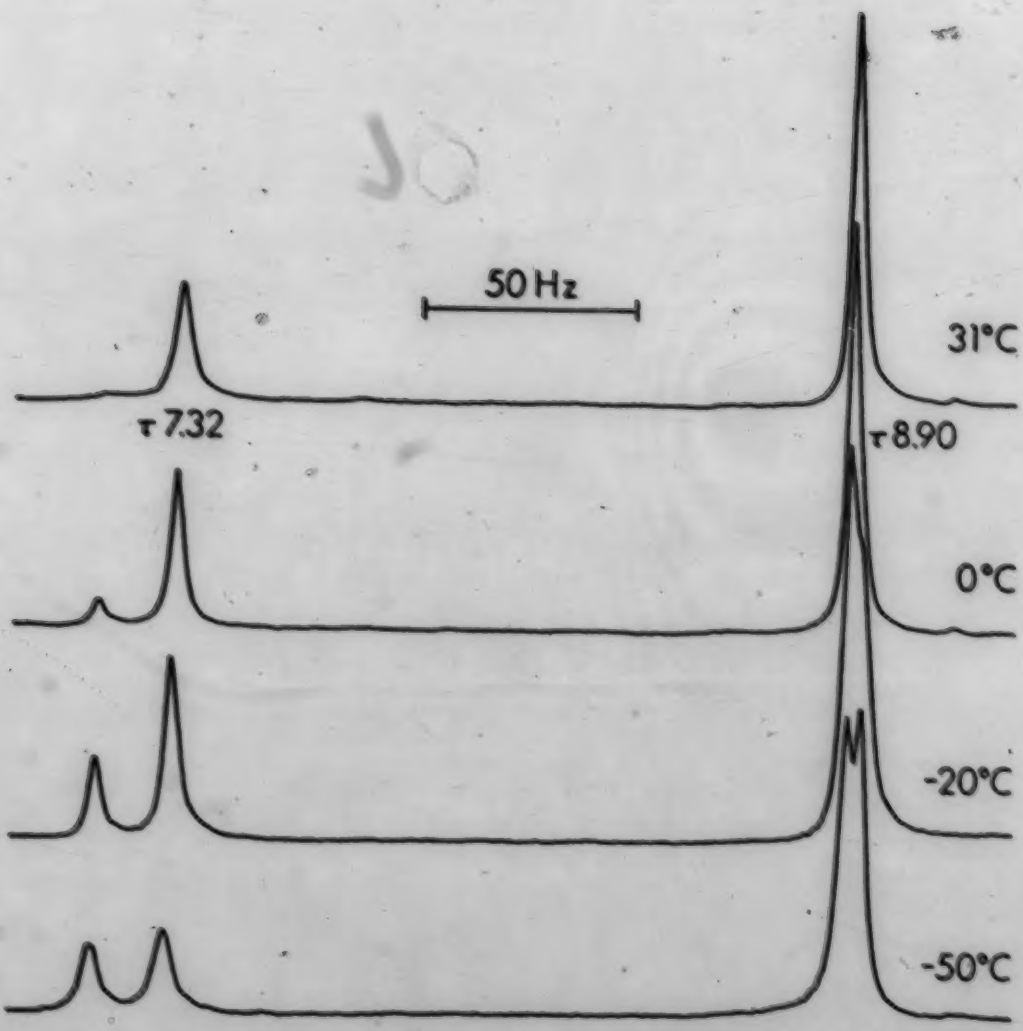


Figure 9. Variable temperature ^{1}H NMR study of $Me_2GeMn(CO)_4COMe$ in CD_2Cl_2.

A typical variable concentration study at a fixed temperature in CD_2Cl_2 is shown in Figure 10. It can be seen that the relative peak intensity is strongly concentration dependent, eliminating the possibility of an intramolecular process. Equilibrium constant values obtained at this temperature from treatment of the results in terms of a dimer-monomer equilibrium were satisfactorily constant. The assignment of peaks due to dimer and monomer is shown in Figure 10, with the peak due to the dimer increasing in intensity as the solution concentration increases. The equilibrium constant, K_{eq}, can be defined as:

$$K_{eq} = \frac{[\text{monomer}]^2}{[\text{dimer}]} \quad \text{for the process dimer} \rightleftharpoons 2 \text{ monomer}$$

where [ ] represents the concentration in mol l^{-1}.

Values of K_{eq} can be easily calculated when it is realised that the integrals of the monomer and dimer NMR peaks are proportional to the masses of monomer and dimer present in solution.* Substituting into the above equation for K_{eq} one can derive the expression:

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*Whereas the monomer peak integral is proportional to the number of monomer molecules, the dimer peak integral is proportional to half the number of dimer molecules, since each dimer contains two C-CH_3 groups. However, each dimer molecule has twice the mass of a monomer molecule and hence peak integrals are proportional to the masses of each species present.

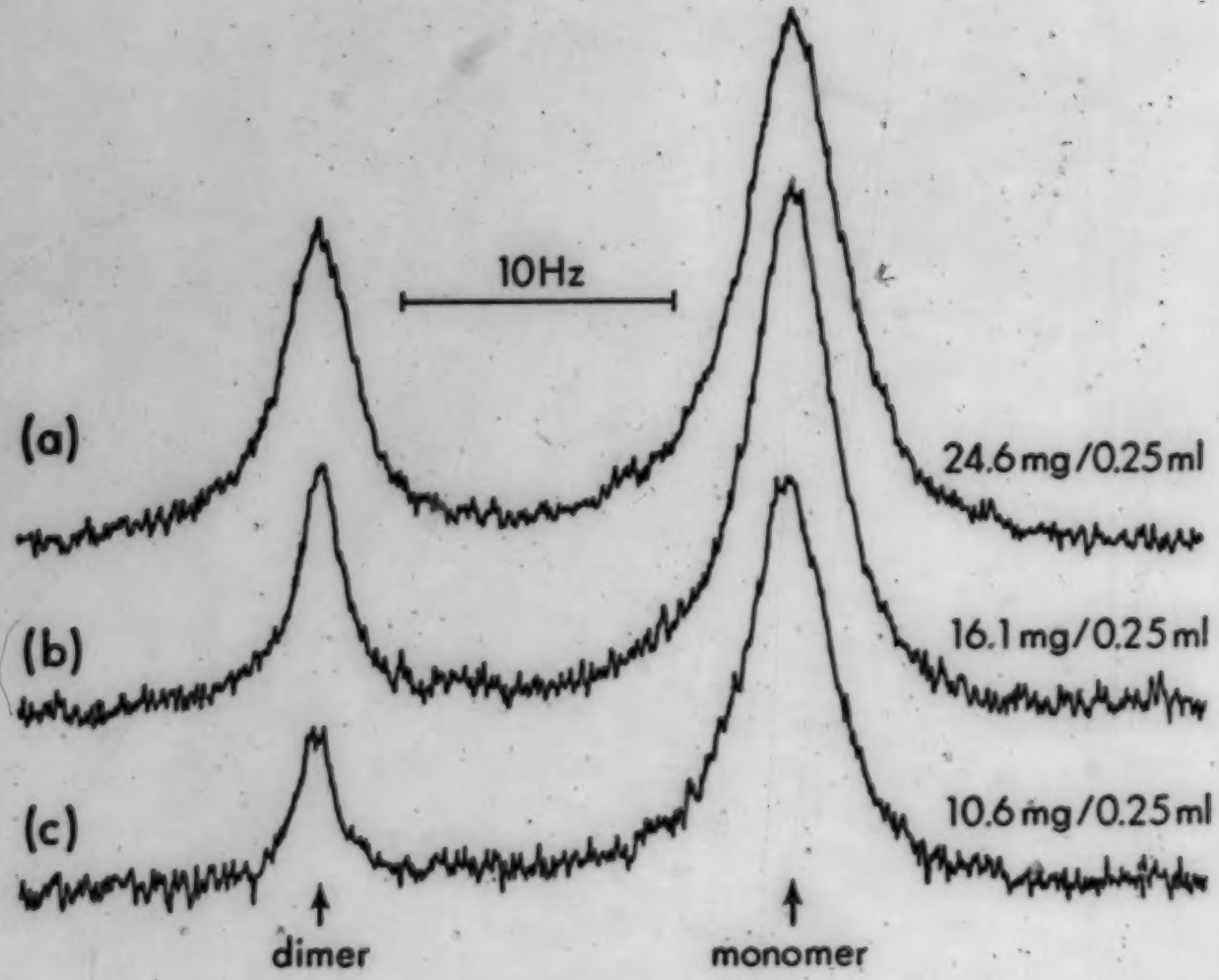

Figure 10. Variable concentration ^{1}H NMR study of $Me_2GeMn(CO)_4COMe$ in CD_2Cl_2 at -30.5°C.

$$K_{eq} = \frac{(Mm)^2}{Md} \cdot \frac{1}{V} \cdot \frac{2}{M.W.m}$$

where Mm = mass of monomer in grams

Md = mass of dimer in grams

V = volume of solution in litres

M.W.m = molecular weight of monomer

Thus, knowing the total mass of material in solution, the solution volume, and monomer and dimer peak integrals, K_{eq} can be calculated. Values of K_{eq} for several variable concentration studies involving the compounds $Me_2GeMn(CO)_4$-COMe and $Me_2GeRe(CO)_4COMe$ are shown in Table V.

A typical variable temperature study for $Me_2GeMn(CO)_4$-COMe at a fixed concentration is shown in Figure 11. Using the integrated peak intensities values of K_{eq} could be calculated at each temperature using the expression for K_{eq} shown above (see Tables VI and VII). Thermodynamic parameters for the dimer-monomer equilibrium could then be obtained by plotting $\ln K_{eq}$ *vs.* $\frac{1}{T}$, where T is the absolute temperature. The values for $\Delta H°$ and $\Delta S°$ quoted in Tables VI and VII were in fact obtained using a least squares computer program rather than a graphical plot; the error limits quoted represent standard deviations. It is important to note that the linear plot of $\ln K_{eq}$ *vs.* $\frac{1}{T}$ observed in this case does not provide unambiguous proof for the existence

TABLE V

VALUES OF K_{eq} FROM VARIABLE CONCENTRATION ^1H NMR STUDIES AT FIXED TEMPERATURES FOR $Me_2GeM(CO)_4COMe$ (M = Mn, Re)

Temperature (°C)	Sample Mass (mg)	Solution Volume (ml CD_2Cl_2)	K_{eq}	Average K_{eq} (standard deviation)
		(1) $Me_2GeMn(CO)_4COMe$		
-29 ±2	14.3	0.40	1.226	
	21.9	0.40	1.132	
	30.4	0.40	1.123	1.14 (±0.08)
	41.6	0.40	1.227	
	49.9	0.40	1.013	
-32 ±2	14.3	0.40	0.720	
	23.1	0.40	0.837	0.78 (±0.05)
	33.1	0.40	0.734	
	47.6	0.40	0.817	
-30.5 ±2	10.6	0.25	1.065	
	16.1	0.25	0.824	0.92 (±0.10)
	24.6	0.25	0.877	
		(2) $Me_2GeRe(CO)_4COMe$		
+31 ±1	4.5	0.25	0.0336	
	6.3	0.25	0.0412	
	8.9	0.25	0.0492	0.040 (±0.005)
	11.0	0.25	0.0381	
	15.7	0.25	0.0381	

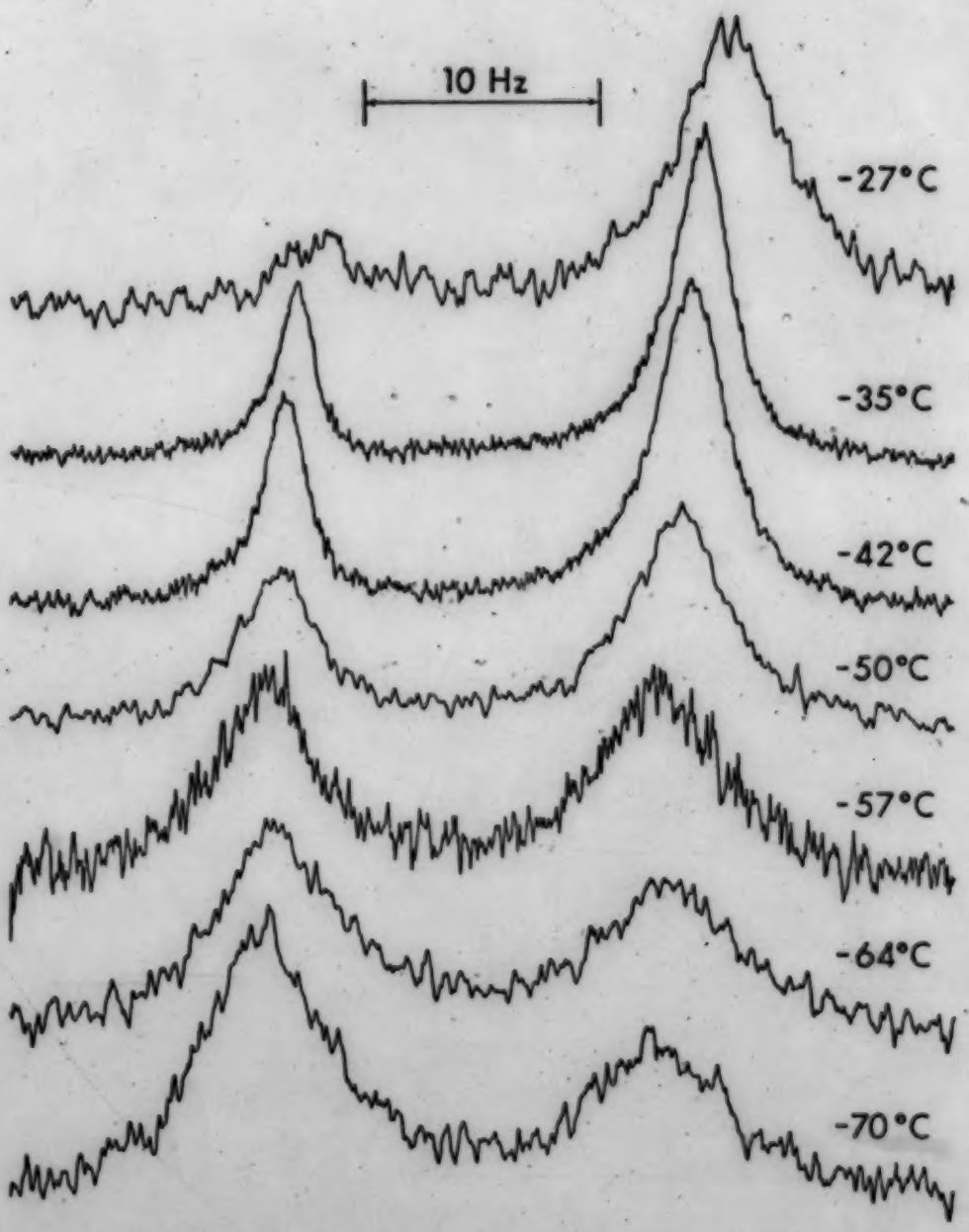

Figure 11. Variable temperature ^{1}H NMR study of $Me_2GeMn(CO)_4COMe$ in CD_2Cl_2, showing an expansion of the C-$\underline{CH}_3$ region only.

TABLE VI

VALUES OF K_{eq}, $\Delta H°$ AND $\Delta S°$ FROM VARIABLE TEMPERATURE ^1H NMR SPECTRA OF $Me_2GeMn(CO)_4COMe$

K_{eq}	T (°K)
Run 1[a]	
5.17	264
1.95	248
0.53	228
0.089	203
Run 2[a]	
1.22	247
0.83	238
0.48	231
0.33	223
0.20	216
0.14	209
0.099	203

$\Delta H°$[b] (standard deviation) = +6.7 (±0.3) Kcal

$\Delta S°$[b] (standard deviation) = +27.9 (±1.4) e.u.

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[a]Concentration 13.2 mg/0.25 ml CD_2Cl_2 for both runs. Solutions made up separately. Combined data from runs 1 and 2 used in calculation of $\Delta H°$ and $\Delta S°$.

[b]Defined for process dimer $\rightleftharpoons$ 2 monomer.

TABLE VII

VALUES OF K_{eq}, $\Delta H°$ AND $\Delta S°$ FROM VARIABLE TEMPERATURE ^1H NMR SPECTRA OF $Me_2GeRe(CO)_4COMe$

K_{eq}		T (°K)
	Run 1[a]	
0.037		308
0.030		304
0.022		298
0.015		293
0.014		288
0.010		283
0.0074		278
0.0052		273
	Run 2[a]	
0.029		304
0.024		301
0.017		296
0.013		291
0.0088		286
0.0089		281
0.0070		276

$\Delta H°$[b] (standard deviation) = +9.0 (±0.4) Kcal

$\Delta S°$[b] (standard deviation) = +22.6 (±1.4) e.u.

[a]Concentration 9.4 mg/0.25 ml CD_2Cl_2 for both runs. Solutions made up separately. Combined data from runs 1 and 2 used in calculation of $\Delta H°$ and $\Delta S°$.

[b]Defined for process dimer⇌2 monomer.

of a dimer-monomer equilibrium. A satisfactory linear graphical plot over the limited temperature range employed (-70 to -25°C) can also be obtained if K_{eq} values are calculated assuming an intramolecular (monomer $\rightleftharpoons$ monomer) process. Thus the variable concentration studies at a fixed temperature are essential in establishing that the process is a dimer-monomer type of intermolecular process.

The above results could obviously equally well apply to, say, a tetramer-dimer as to a dimer-monomer equilibrium. The fact that the latter process is in fact involved has been confirmed by a solution molecular weight determination of $Me_2GeMn(CO)_4COMe$ under conditions where little of the associated form is present (11.4 mg ml^{-1}, 37°, CH_2Br_2 solution). The osmometric molecular weight was found to be 318 which is very close to the calculated value for the monomer of 313. Solution infrared spectra which are carried out using even less concentrated solutions show only one species present in solution and this must also be monomeric.

Reinforcement of the idea of a dimer-monomer equilibrium in the case of $Me_2GeRe(CO)_4COMe$ has come from X-ray crystallography. Recrystallization of a sample of the complex from a fairly concentrated solution at -15°C (conditions under which the associated form would predominate) yielded crystals suitable for an X-ray crystallographic study. This has revealed the dimeric form of the complex (see Chapter II).

The dimeric form is more favoured for the rhenium derivative than for its manganese analog at a given temperature and solution concentration. Hence, whereas in the manganese case variable concentration studies were carried out at *ca.* -30° in order for an appreciable amount of dimer to be present, the rhenium system could be studied at room temperature (see Table V). It can be seen (Tables VI and VII) that both $\Delta H°$ and $\Delta S°$ terms favour a higher proportion of dimer in the rhenium case, compared with its manganese analog under the same conditions. It is possible that steric effects may be of importance here as there may be greater ring strain in the four-membered heterocycle containing rhenium compared with manganese, making dimer formation more favourable in the former case.

Osmometric molecular weight determinations for the complex of empirical formula $Me_2SnRe(CO)_4COMe$ indicate that it is essentially completely dimeric at ambient temperature even in dilute solutions. (The molecular weight calculated for the dimer is 980; values found at concentrations of 4.863 and 6.519 mg ml^{-1} in CH_2Cl_2 at ambient temperature were 956 and 984 respectively). In a ^1H NMR spectrum in CD_2Cl_2 at ambient temperature signals due to only one species (presumably dimer) were observed (Figure 8) and an attempt to obtain spectra at higher temperatures in $CDCl_3$ in the hope of observing some monomer was inconclusive, since at the low concentration employed

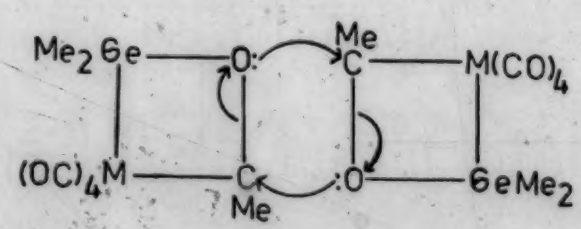
(the complex is not very soluble in CD_2Cl_2 or $CDCl_3$) the signal-to-noise ratio rapidly decreased above ambient temperature.

It has been observed in studies of the dimer-monomer equilibria that peak coalescence does not occur as the temperature is increased, rather the relative intensity of the peaks due to monomer and dimer change. As explained above, in all but the most concentrated solutions no dimer is visible at ambient temperature in the case of $Me_2GeMn(CO)_4COMe$. It appears that as the temperature is raised to room temperature the peak due to the dimer simply decreases in intensity and disappears into the base line without the occurrence of peak coalescence. If peak coalescence were occurring one would expect to see line broadening as the temperature rises, but in fact the lines become sharper (see Figure 11). The line broadening observed at lower temperatures arises from viscosity effects in solution, as shown by the fact that the peak due to the internal tetramethylsilane reference also broadens at lower temperatures. Viscosity broadening is not observed in the case of $Me_2GeRe(CO)_4COMe$; more dilute solutions were employed at temperatures between 0° and +35°C to study its dimer-monomer equilibrium, these conditions being necessary for the observation of appreciable amounts of monomer. The fact that peak coalescence does not occur in either the manganese

or rhenium case establishes that the interconversion of monomer and dimer is slow on the NMR time-scale at ambient temperature.

Possible Mechanisms for Interconversion

Two speculative schemes for the formation of a molecule of dimer from two molecules of monomer are shown in 20 and 21. These postulate nucleophilic attack of the carbene



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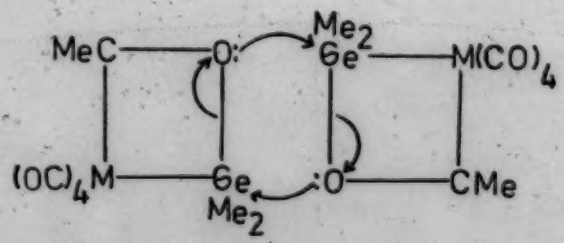

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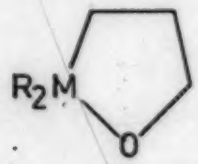
oxygen atom upon germanium or carbene carbon atoms in another monomer molecule. Possibilities involving the breakage of metal to carbene carbon or metal to germanium bonds appear to be less likely.

It would be expected that the oxygen atom in the four-membered monomeric heterocycle might retain some nucleophilic character despite the donation of some of its lone pair electron density to the carbene carbon atom. Indeed, it is thought that in the aminolysis reaction of $Cr(CO)_5C(OMe)Ph$ with primary amines to form aminocarbene complexes (a reaction of the type I-2) the initial step of the reaction involves hydrogen bonding between the oxygen atom of the methoxycarbene group and a hydrogen atom of an amine or solvent molecule.[67]

The electrophilic character of carbene carbon atoms has been clearly shown in several reactions. In Chapter I their reactivity towards such nucleophiles as phenyllithium[16] and phosphines[22-4] has been described. The electrophilic character of the germanium atom in the new heterocycles has been shown by reactions with methyllithium and methoxide ion described in Chapter IV.

As pointed out earlier, no precedent exists in the realm of metal carbene chemistry for a dimer-monomer process of this type. Very recently however organo-silicon, -germanium and -tin heterocycles of the type 22 have been

postulated to exist in associated forms, based on infrared evidence in the carbon-oxygen stretching region.[68] The process is thought to be solvent and temperature dependent and to occur via coordination of the oxygen atom to the



22

atom, M, of another molecule, in a manner analogous to 21 above.

Despite the fact that possibilities such as 20 and 21 appear feasible, no positive evidence to support or distinguish them exists. If either of these pathways is in effect one might expect that the addition of a Lewis base such as diethyl ether might have a marked effect on the position of the equilibrium. However, it has been found that addition of an approximately equimolar amount of ether (equimolar based on the complex $Me_2GeMn(CO)_4COMe$ being entirely monomeric), increases the equilibrium constant K_{eq} only from 0.46 to 0.78 at -38.5 (±2) and -37 (±2) °C respectively. Considering that K_{eq} values are only reproducible in single determinations to *ca.* ±10% at a given

temperature and the fact that the slightly higher temperature at which the spectrum was recorded in the presence of ether would cause a slight raising of the value of K_{eq}, the observed change is rather minor. Also in this regard, some interaction of chlorinated solvents with the carbene heterocycles cannot be eliminated. This might rationalize the small effect of the addition of diethyl ether in the presence of a large excess of CD_2Cl_2, and might also be consistent with the earlier observation (Chapter II) that the cyclic carbenes are all much more stable in chlorinated solvents than in hydrocarbon solutions.

EXPERIMENTAL

The complexes of empirical formulae $Me_2GeMn(CO)_4COMe$, $Me_2GeRe(CO)_4COMe$ and $Me_2SnRe(CO)_4COMe$ were prepared as described in Chapter II. Samples for ^1H NMR work were prepared by carefully weighing the desired amount of material and adding a known amount of nitrogen-saturated CD_2Cl_2 from a syringe. After dissolving the solid sample the solution was transferred to an NMR tube using a disposable pipette. The tube was quickly filled with nitrogen and capped after the addition of one drop of tetramethylsilane. (The unknown volume of this drop and small evaporation losses of the volatile solvent during the preparation of the sample are potential sources of small errors in values of K_{eq}).

The variable temperature and variable concentration ^1H NMR spectra were recorded using a Varian HA 100 instrument. In the case of $Me_2GeMn(CO)_4COMe$ the temperature was regulated using a Varian V-4341/V-6057 temperature control unit, and the temperature accurately measured before and after running each spectrum using a thermocouple. A Bruker B-ST 100/700 temperature control unit was employed for spectra of $Me_2GeRe(CO)_4COMe$. This unit contains an internal thermocouple and no external calibration was therefore required. Peak integrals were recorded for all

spectra and K_{eq} values could be calculated as described in the text. Two independent variable temperature runs at a fixed concentration were carried out for each complex. The K_{eq} data from the two independent runs were combined and a least squares program was used to calculate $\Delta H°$ and $\Delta S°$, as described in the text.

Osmometric molecular weights were determined in the microanalytical laboratory of this Department and by Alfred Bernhardt Microanalytisches Laboratorium, West Germany.

CHAPTER IV

The Reactivity of Cyclic Germoxycarbene Complexes of Manganese and Rhenium Towards Nucleophiles

Introduction

As described in Chapter I, transition metal carbene complexes have been found to react with nucleophiles such as phosphines[22-4] and phenyllithium[16] with attack occurring at the carbene carbon atom. The novel cyclic germoxycarbene complexes described in Chapter II might also be expected to show this type of behaviour. In the preliminary studies described below it has been found, however, that products from reactions of methyllithium or methoxide ion with the cyclic complexes can be rationalised in terms of nucleophilic attack at the germanium atom. On the basis of these interesting preliminary results it is hoped that further reactions of this type will be studied.

Synthesis and Characterisation of Products

The Reaction of $Ph_2GeRe(CO)_4COMe$ with MeLi

The cyclic complex of empirical formula $Ph_2GeRe(CO)_4COMe$* reacts rapidly with a slight excess of methyllithium in ether to give a lithium acylate presumed to be *cis*-$Ph_2MeGeRe(CO)_4C(OLi)Me$. Subsequent treatment with Et_3OBF_4 in water yields the novel carbene complex formulated as *cis*-$Ph_2MeGeRe(CO)_4C(OEt)Me$ (IV-1). The suggested formulation of the product

$$Ph_2GeRe(CO)_4COMe + MeLi \xrightarrow{\text{ether}} cis\text{-}Ph_2MeGeRe(CO)_4C(OLi)Me \xrightarrow[\text{water}]{Et_3OBF_4} cis\text{-}Ph_2MeGeRe(CO)_4C(OEt)Me \qquad \text{IV-1}$$

is fully consistent with its mass and infrared spectra, and with analytical data (see Tables VIII and IX and Figure 12). The attachment of a methyl group to germanium in the final product is further supported by a ^1H NMR spectrum, which reveals a methyl singlet at τ 9.10 (see Table X). This can be compared with values of τ 8.93 and τ 9.41 respectively for methyl groups bound to germanium in the complexes $Me_2GeRe(CO)_4COMe$ and $Me_3GeRe(CO)_5$ reported in Chapter II.

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*In reactions of this type it is not known whether the cyclic carbene complexes undergo nucleophilic attack in their monomeric or dimeric forms, or both.

TABLE VIII

CARBONYL STRETCHING FREQUENCIES, AND MASS SPECTRAL PARENT IONS

FOR DERIVATIVES OF $Ph_2GeM(CO)_4COMe$ (M = Mn, Re)

Compound	Mass Spectral Parent Ion (m/e)[a]	Carbonyl Stretching Frequencies (cm^{-1})[e,f]
cis-$Ph_2MeGeRe(CO)_4C(OEt)Me$	612[b]	2074 (m), 1994 (m), 1971 (vs), 1966 (s, sh)
cis-$Ph_2MeGeMn(CO)_4C(OEt)Me$	482[c]	2052 (m), 1984 (m), 1965 (vs), 1959 (s, sh)
cis-$Ph_2FGeMn(CO)_4C(OEt)Me$	486[d]	2066 (m), 1995 (m), 1978 (vs), 1974 (s, sh)
[*cis*-$Ph_2MeGeMn(CO)_4C(O)Me$][Et_4N]	—	2019 (m), 1930 (vs), 1917 (vs), 1897 (s)
[*cis*-$Ph_2(HO)GeMn(CO)_4C(O)Me$][Et_4N]	—	2025 (m), 1943 (s, sh), 1931 (vs), 1910 (s, sh)

[a]Most abundant peak of isotope combination pattern of parent ion reported. Parent ions show expected isotope combination patterns.

[b]The spectrum, recorded at a source temperature of 45°C, reveals the presence of an impurity of higher molecular weight; the observed spectrum is, therefore, complex. Intense peaks at m/e 597 due to loss of a methyl group from the parent ion, and at m/e 243 due to Ph_2MeGe^+ are observed.

[c]Shows competing losses of carbonyls and a methyl group from the parent ion. Stepwise loss of four carbonyl groups observed. Very intense peak at m/e 243 due to Ph_2MeGe^+.

[d]Recorded at a source temperature of 85°C. Spectrum showed competing losses of a fluorine atom and carbonyl groups from the parent ion. Stepwise loss of four carbonyl groups observed. At a source temperature of 60°C spectrum of volatile impurities observed, with the two peaks of highest mass at m/e 442 and 454. For that at m/e 442, peaks due to loss of one, three, and five carbonyl groups from this parent can be assigned; an intense peak at m/e 247, due to Ph_2FGe^+, further suggests that the peak at m/e 442 might be due to $Ph_2FGeMn(CO)_5$. The ion at m/e 454 corresponds to the mass of $Ph_2(MeO)GeMn(CO)_5$, but this ion shows only the loss of two, three, and four carbonyl groups.

[e]Cyclohexane solvent for neutral complexes, dichloromethane for salts.

[f]Abbreviations as in Table I.

TABLE IX

ANALYTICAL DATA, COLOURS, MELTING POINTS, AND YIELDS FOR DERIVATIVES OF $Ph_2GeM(CO)_4COMe$ (M = Mn, Re)

Compound	Colour	M.P.(°C)	% Yield	Calcd. % C	Calcd. % H	Found %[a] C	Found %[a] H
cis-$Ph_2MeGeRe(CO)_4C(OEt)Me$	White	54-7	44	41.20	3.46	40.19	3.38
cis-$Ph_2MeGeMn(CO)_4C(OEt)Me$	Yellow	oil	28	52.45	4.40	50.55	4.23
cis-$Ph_2FGeMn(CO)_4C(OEt)Me$	Colourless	62-4	14	49.54	3.74	49.44	3.95
[*cis*-$Ph_2MeGeMn(CO)_4C(O)Me$][Et_4N][b]	Pale Yellow	89-91	2	55.71	6.23	54.36	6.30
[*cis*-$Ph_2(HO)GeMn(CO)_4C(O)Me$][Et_4N][c]	Pale Yellow	98-100	50	53.47	5.87	55.08	5.81

[a]C, H, N analyses carried out in duplicate by the Microanalytical Laboratory of this Department (mean value given).

[b]Calcd.: N = 2.41. Found: N = 2.69.

[c]Calcd.: N = 2.40. Found: N = 2.64.

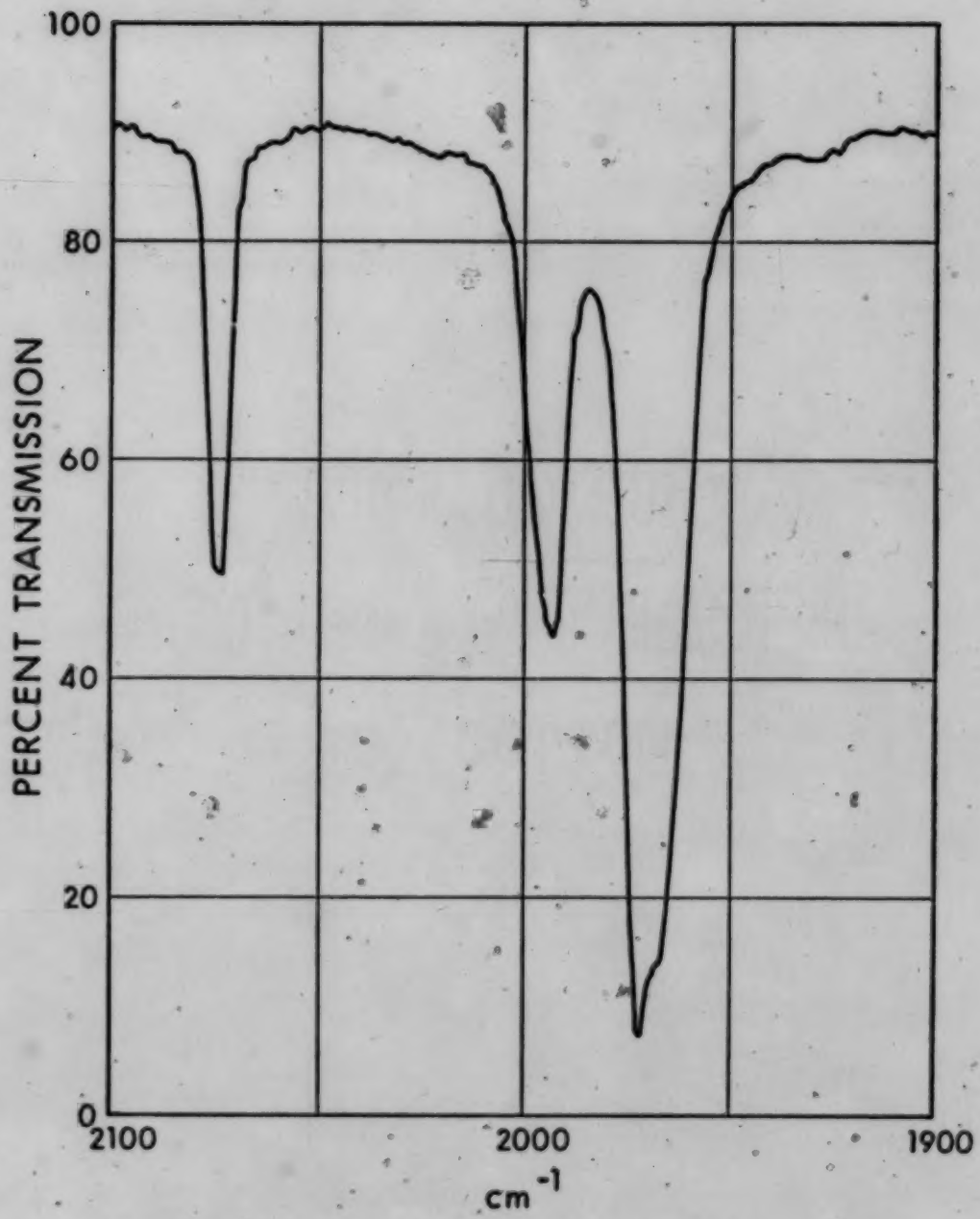

Figure 12. Infrared spectrum [ν(CO) region] of *cis*-$Ph_2MeGeRe(CO)_4C(OEt)Me$ in *cyclo*hexane.

TABLE X

^{1}H NMR DATA FOR DERIVATIVES OF $Ph_2GeM(CO)_4COMe$ (M = Mn, Re)

Compound	Chemical Shift (τ-value)[a,b]				
	C-$\underline{CH}_3$[c]	Ge-$\underline{CH}_3$[c]	O-$\underline{CH}_2$-CH_3[d]	O-CH_2-$\underline{CH}_3$[e]	Solvent
cis-$Ph_2MeGeRe(CO)_4C(OEt)Me$	7.68	9.10	6.10	8.67	$CDCl_3$
cis-$Ph_2MeGeMn(CO)_4C(OEt)Me$	7.58	9.05	6.18	8.62	$CDCl_3$
cis-$Ph_2FGeMn(CO)_4C(OEt)Me$	7.19	—	5.88	8.62	$CDCl_3$
[*cis*-$Ph_2(HO)GeMn(CO)_4C(O)Me$][Et_4N][f]	7.62	—	—	—	$(CD_3)_2CO$

[a]Relative to internal TMS at 10 τ. Peak integrals consistent with suggested formulations.

[b]Ph resonance complex multiplet at *ca.* 2.5-3.0 τ in all cases.

[c]Singlet.

[d]Quartet.

[e]Triplet.

[f]O-$\underline{H}$ at τ 5.74 (singlet); N-$\underline{CH}_2$-CH_3 at τ 6.66 (quartet); N-CH_2-$\underline{CH}_3$ at τ 8.72 (triplet of triplets).

Thus, the product of IV-1 appears to result from methyllithium attack at germanium, although there is no evidence to establish that the germanium atom is the site of initial attack.

The Reaction of $Ph_2GeMn(CO)_4COMe$ with MeLi

The reaction of $Ph_2GeMn(CO)_4COMe$ with methyllithium is rather more complex and further work is warranted on this system. The use of a 5.5:1 mole ratio of MeLi to $Ph_2GeMn(CO)_4COMe$ in ether, followed by treatment with Et_3OBF_4 in water, yields exclusively *cis*-$Ph_2MeGeMn(CO)_4C(OEt)Me$ as a yellow oil, in a reaction analogous to IV-1. Repeated attempts have failed to provide a sample of the highest analytical purity (see Table IX), but infrared and mass spectra, and particularly a ^1H NMR spectrum have allowed an unambiguous structural assignment to be made (see Tables VIII and X and Figures 13 and 14). The ^1H NMR spectrum reveals a singlet at τ 9.05 due to the methyl group attached to germanium. The acylate precursor to the final product has been isolated in low yield as a tetraethylammonium salt, [*cis*-$Ph_2MeGeMn(CO)_4C(O)Me][Et_4N]$, which has been analysed (Table IX), and whose infrared spectrum resembles that of the complex [*cis*-$Ph_3GeMn(CO)_4C(O)Me][Et_4N]$ described in Chapter V. Treatment of [*cis*-$Ph_2MeGeMn(CO)_4C(O)Me][Et_4N]$ with Et_3OBF_4 in dichloromethane yields *cis*-$Ph_2MeGeMn(CO)_4C(OEt)Me$.

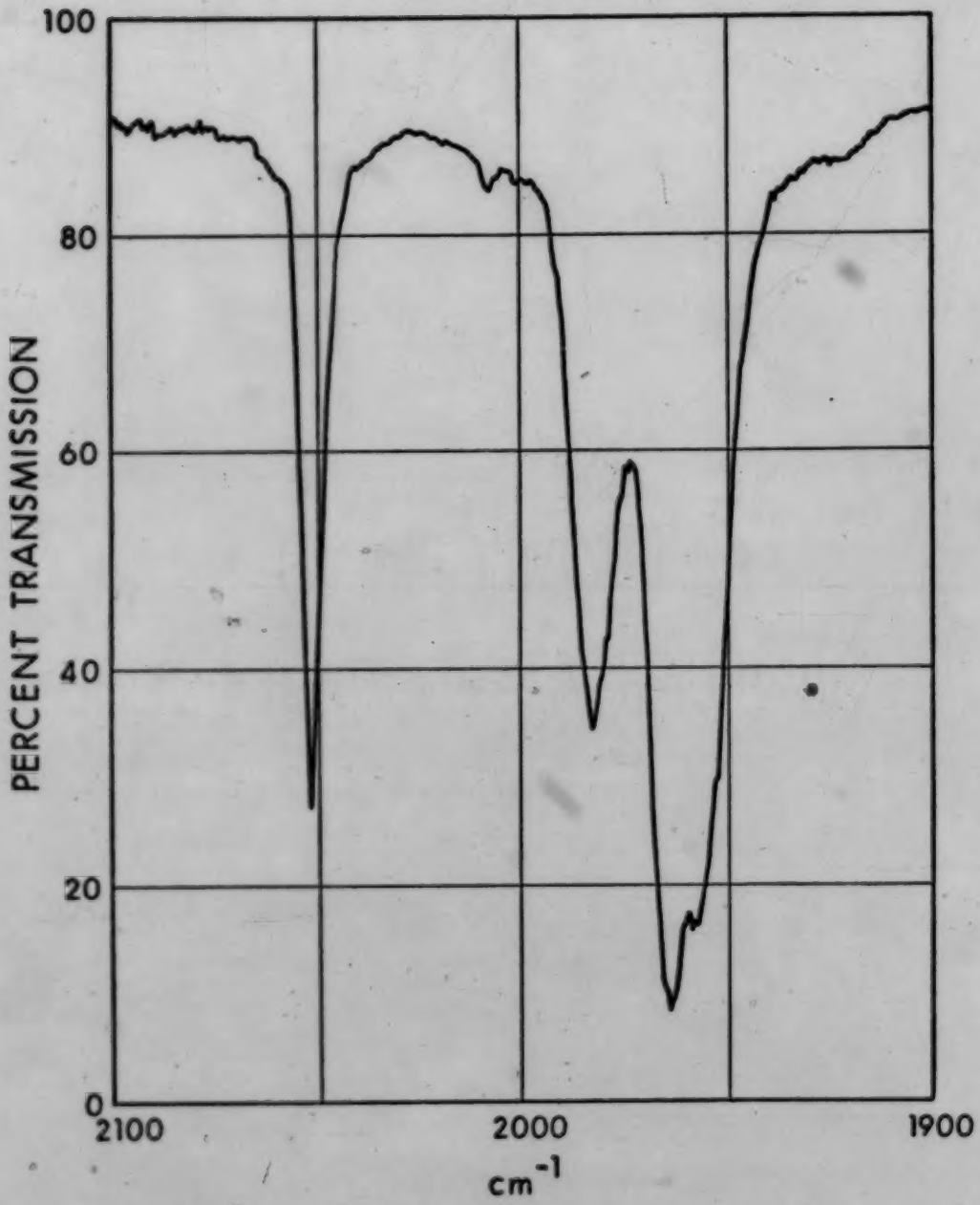

Figure 13. Infrared spectrum [ν(CO) region] of *cis*-$Ph_2MeGeMn(CO)_4C(OEt)Me$ in *cyclo*hexane.

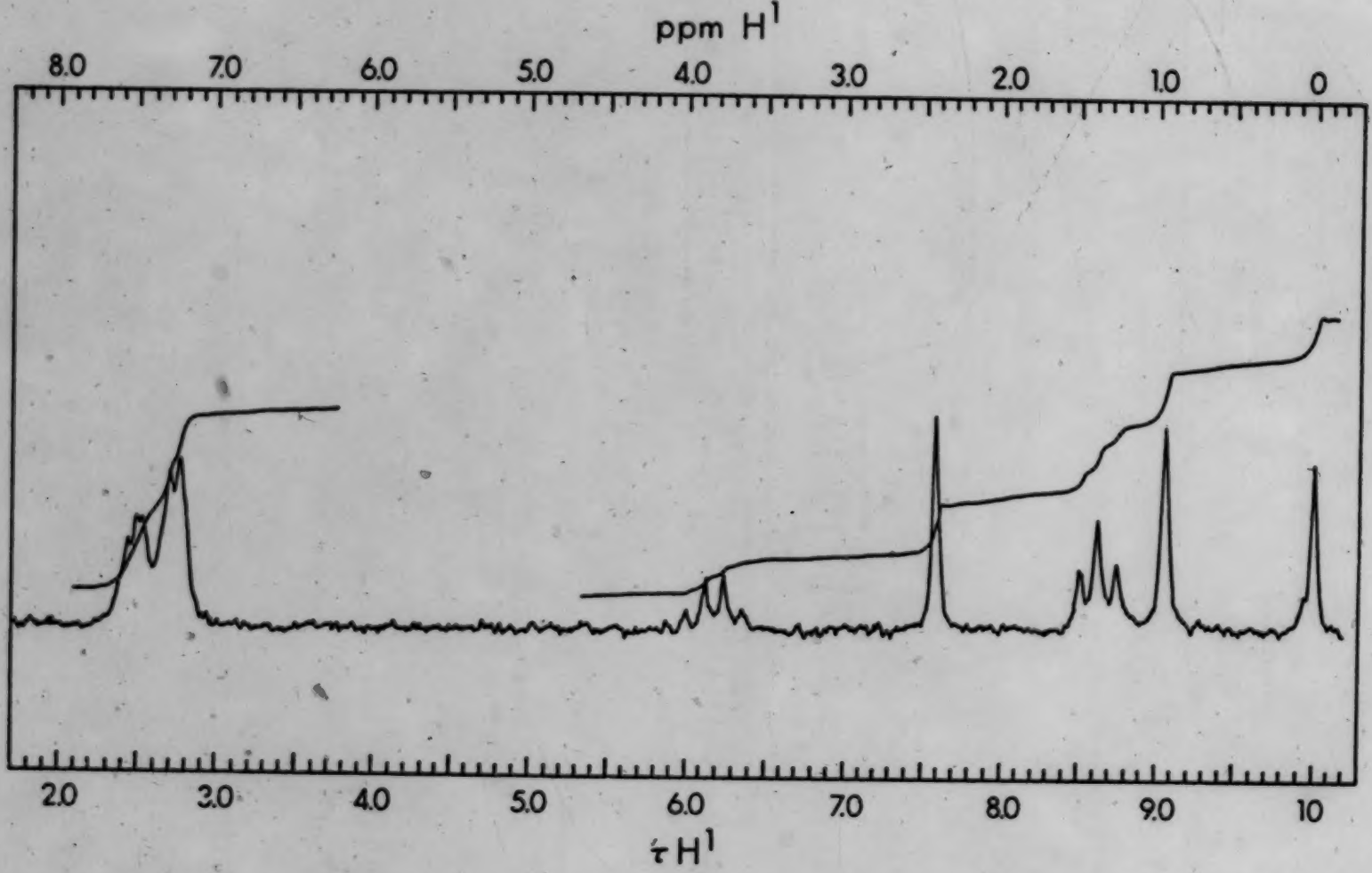

Figure 14. ^{1}H NMR spectrum of *cis*-$Ph_2MeGeMn(CO)_4C(OEt)Me$ in $CDCl_3$.

If an equimolar quantity of methyllithium is added to $Ph_2GeMn(CO)_4COMe$ in ether, infrared bands due to two anionic species are observed, one of them being *cis*-$Ph_2MeGeMn(CO)_4C(OLi)Me$.* Addition of a less-than-equimolar quantity of methyllithium to $Ph_2GeMn(CO)_4COMe$ in ether appears to increasingly favour the unidentified anion as the proportion of methyllithium is decreased, while also leaving more unreacted starting material. Upon further addition of methyllithium the unidentified anion is converted into *cis*-$Ph_2MeGeMn(CO)_4C(OLi)Me$. Treatment of the unidentified anion with Et_3OBF_4 yields an impure yellow oil, whose infrared and mass spectra closely resemble those of a sample of $Ph_2FGeMn(CO)_4C(OEt)Me$, a novel complex whose synthesis by another route is described below.

The Reaction of $Ph_2GeMn(CO)_4COMe$ with NaOMe

The reaction of $Ph_2GeMn(CO)_4COMe$ with excess sodium methoxide in methanol proceeds cleanly, and infrared spectra recorded in dichloromethane after removal of the methanol solvent indicate formation of an anion. If an equimolar quantity of sodium methoxide is employed, the

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*Most of the infrared bands appear to overlap, but the highest energy band of each species is clearly visible. These peaks are observed at 2038 and 2026 cm^{-1} in diethyl ether and the latter is assigned to *cis*-$Ph_2MeGeMn(CO)_4C(OLi)Me$. The structure of the other species is not known.

same anion is produced and some starting material remains. Treatment of the anion with tetraethylammonium bromide in water does not yield [*cis*-$Ph_2(MeO)GeMn(CO)_4C(O)Me][Et_4N]$, but a complex believed to be the first hydroxygermanium-transition metal derivative, [*cis*-$Ph_2(HO)GeMn(CO)_4C(O)Me][Et_4N]$.* It seems feasible that the reaction of sodium methoxide with $Ph_2GeMn(CO)_4COMe$ might initially result in a methoxygermyl derivative and that subsequent reaction with water replaces a methoxy group by a hydroxy group, as shown in IV-2. Some physical properties of the hydroxygermyl complex are given

$$Ph_2GeMn(CO)_4COMe + MeONa \xrightarrow{MeOH} [cis\text{-}Ph_2(MeO)GeMn(CO)_4C(ONa)Me] \xrightarrow[water]{Et_4NBr} [cis\text{-}Ph_2(HO)GeMn(CO)_4C(O)Me][Et_4N] \qquad \text{IV-2}$$

in Tables VIII-X, and its solution infrared spectrum in the carbonyl region is shown in Figure 15. The presence of an O-H group in the molecule is confirmed by a ^1H NMR spectrum in acetone-d_6 which reveals a signal at τ 5.74, integrating as one proton, which disappears upon treatment with D_2O (see Figures 16 and 17). An infrared spectrum in Nujol shows bands at 3290 and 1570 cm^{-1} assignable to ν(OH) and $\nu(C\text{-}O^-)$.

The methoxygermyl intermediate postulated in IV-2, upon treatment with Et_3OBF_4 in water, yields the novel carbene

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*The first hydroxysilyl-transition metal complex, $(\eta\text{-}C_5H_5)Fe(CO)_2SiMe_2(OH)$, was recently prepared in this laboratory.[69]

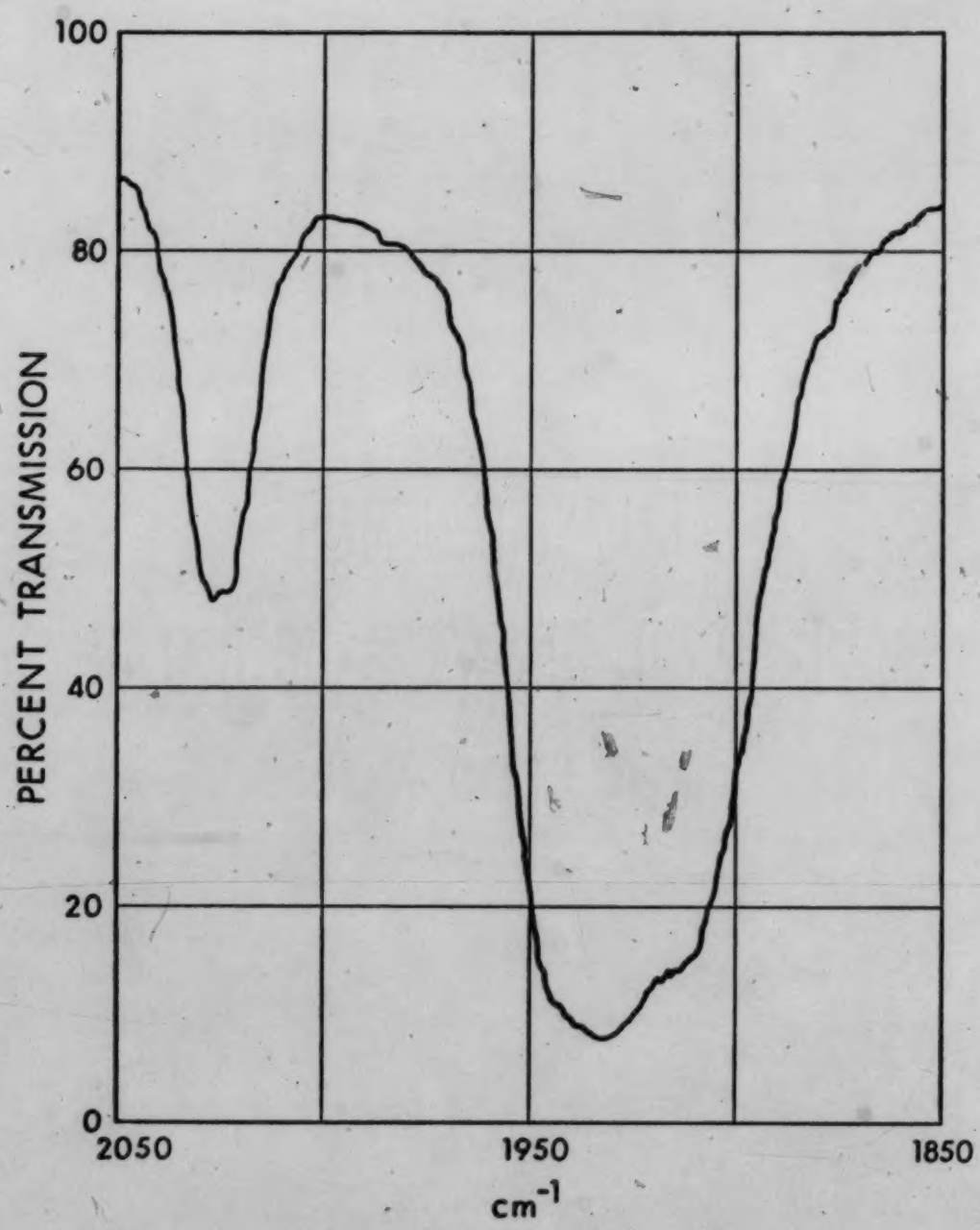


Figure 15. Infrared spectrum [ν(CO) region] of [*cis*-$Ph_2(HO)GeMn(CO)_4C(O)Me][Et_4N]$ in CH_2Cl_2.

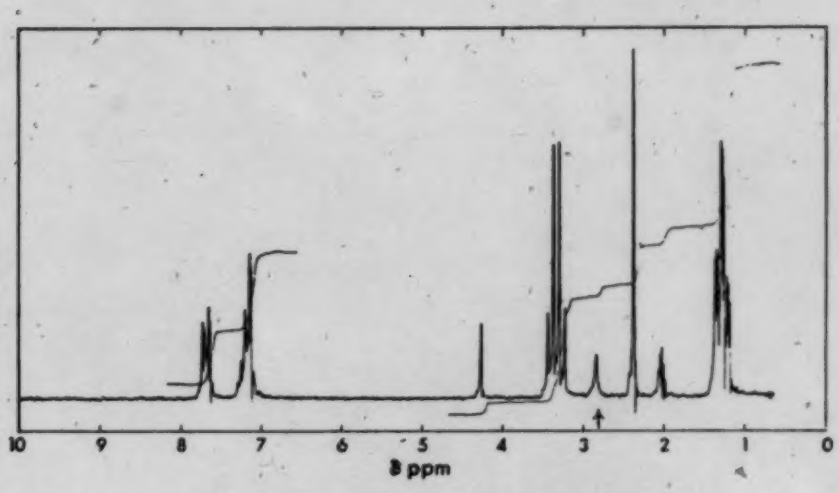


Figure 16

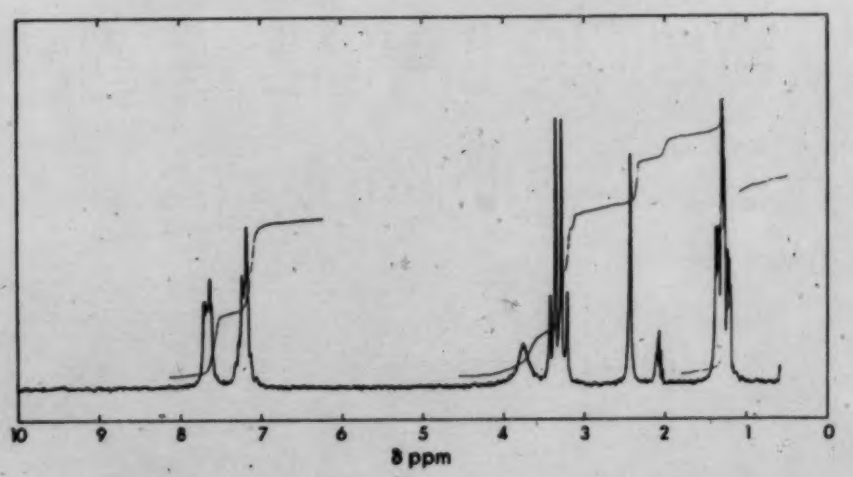


Figure 17

Figure 16. ^{1}H NMR spectrum of [*cis*-$Ph_2(HO)GeMn(CO)_4C(O)Me$] [Et_4N] in acetone-d_6 (the peak indicated by the arrow was present in a spectrum of the solvent and is thought to be due to water).

Figure 17. ^{1}H NMR spectrum of [*cis*-$Ph_2(HO)GeMn(CO)_4C(O)Me$] [Et_4N] in acetone-d_6, after treatment with D_2O.

complex *cis*-$Ph_2FGeMn(CO)_4C(OEt)Me$, as shown in IV-3. It is of course possible, based on reaction IV-2, that the reactive

$$[cis\text{-}Ph_2(MeO)GeMn(CO)_4C(ONa)Me] \xrightarrow[water]{Et_3OBF_4} cis\text{-}Ph_2FGeMn(CO)_4C(OEt)Me \qquad \text{IV-3}$$

species involved in IV-3 could be a hydroxygermyl complex generated by reaction with water prior to addition of the Et_3OBF_4. Spectroscopic properties and analytical results for *cis*-$Ph_2FGeMn(CO)_4C(OEt)Me$ are presented in Figures 18 and 19 and Tables VIII-X. It has been shown by Marks *et al.* that the BF_4^- ion can act as a fluorine source when $AgBF_4$ is used as a reagent in reactions of the type I-8.[36,37] However, it is also possible that impurities in the Et_3OBF_4, e.g., HF, might also be responsible for fluorination of the germanium atom.

It is apparent from the above discussion that several features of the reactions described require further study. It is hoped that these reactions and reactions of the cyclic carbene complexes with other nucleophiles, both anionic and neutral, will yield further interesting results.

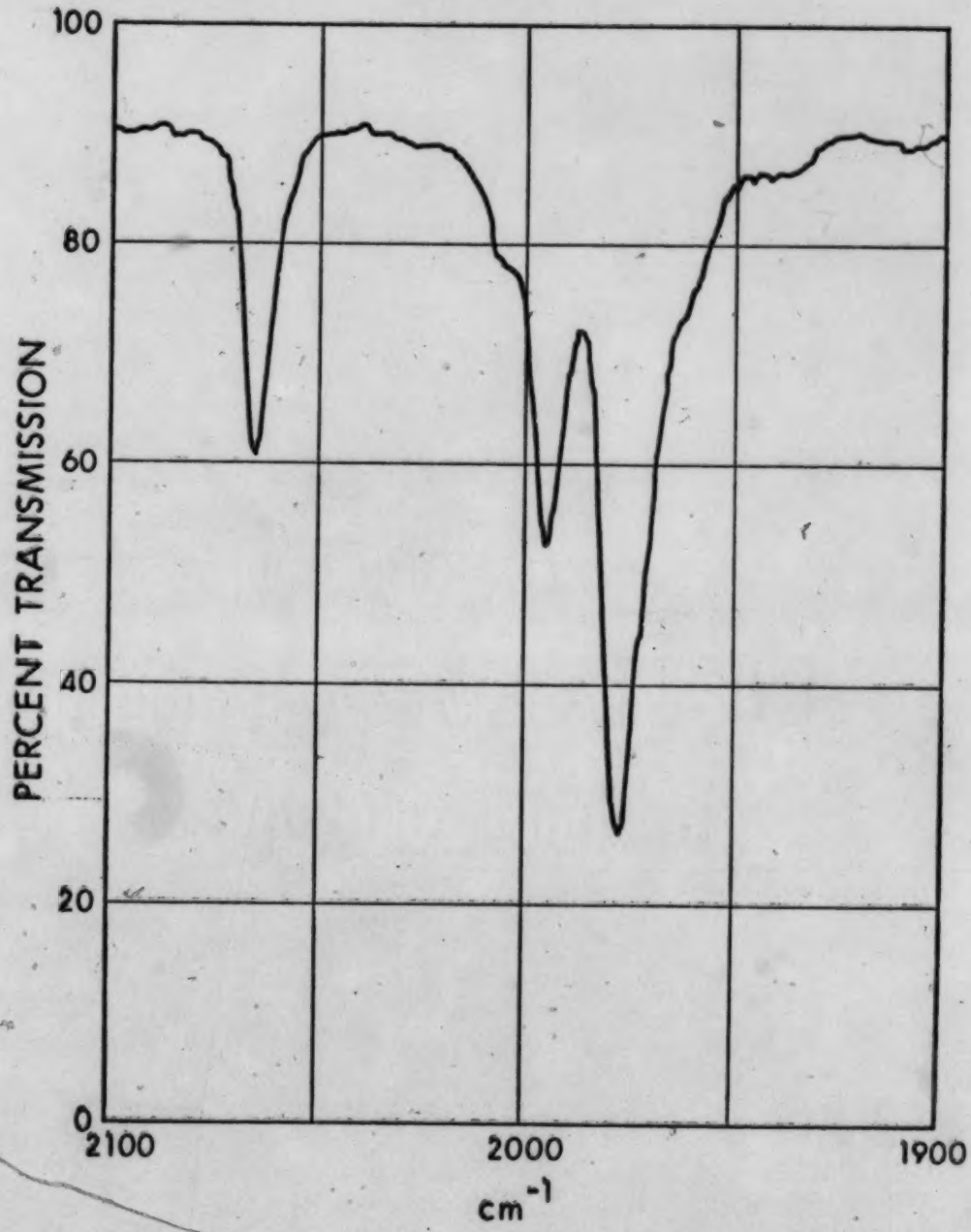


Figure 18. Infrared spectrum [ν(CO) region] of *cis*-$Ph_2FGeMn(CO)_4C(OEt)Me$ in *cyclo*hexane. (The peak at 2007 cm^{-1} is assigned to an impurity).

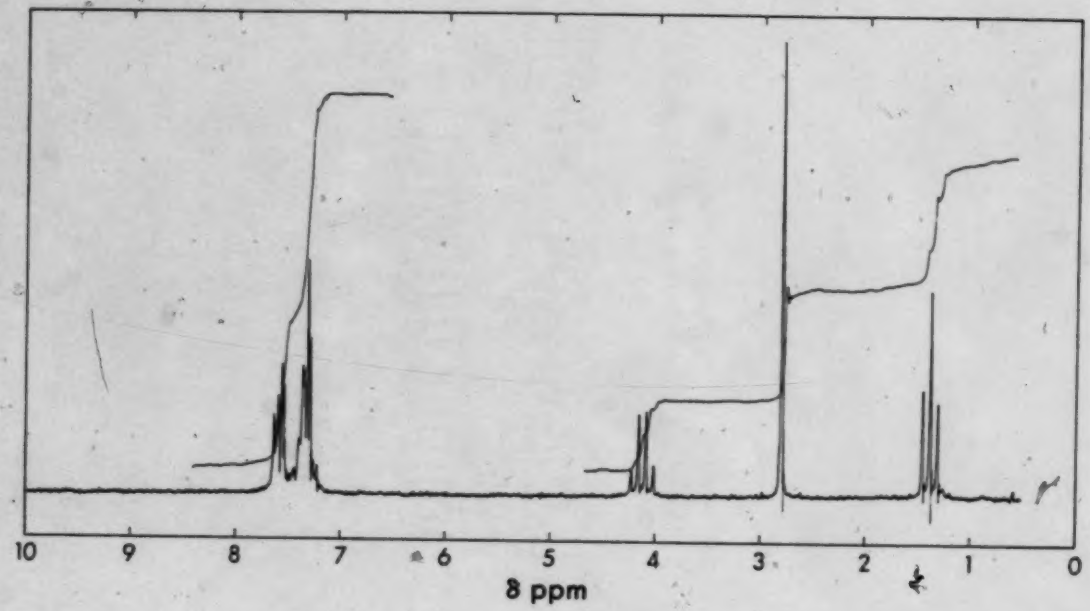


Figure 19. ^{1}H NMR spectrum of *cis*-$Ph_2FGeMn(CO)_4C(OEt)Me$ in $CDCl_3$.

EXPERIMENTAL

Reactions were carried out under a static nitrogen atmosphere, using solvents previously saturated with nitrogen. Diethyl ether, dichloromethane, and methanol were dried by distillation from calcium hydride, phosphorus pentoxide, and magnesium, respectively.

Solutions of methyllithium in ether were obtained from Alfa Inorganics Inc., Beverly, Mass.; tetraethylammonium bromide and chloride were supplied by Eastman Organic Chemicals, Rochester, N.Y.; sodium methoxide was obtained from Fischer Scientific Company, Fair Lawn, N.J.; Et_3OBF_4 was purchased from Fluka AG, Switzerland; sodium sulphate (anhydrous) and chromatographic alumina (calcined) were obtained from BDH Chemicals Ltd., Poole, England, and BDH (Canada) Ltd., Toronto, respectively. The compounds $Ph_2GeMn(CO)_4COMe$ and $Ph_2GeRe(CO)_4COMe$ were prepared as described in Chapter II.

Microanalyses were performed in the Microanalytical Laboratory of this Department. Melting points, and infrared, mass and ^1H NMR spectra were recorded as described in Chapter II.

Where approximate pH values are mentioned in the following reactions, they were measured using "pHydrion" indicator papers, purchased from the Micro Essential Laboratory, Brooklyn, N.Y.

Reaction of $Ph_2GeRe(CO)_4COMe$ with (1) MeLi, (2) Et_3OBF_4

To $Ph_2GeRe(CO)_4COMe$ (0.19 g, 0.33 mmol) in diethyl ether (15 ml) was added from a syringe a solution of 1.5 M MeLi in ether (0.23 ml, 0.34 mmol). An immediate colour change from colourless to pale yellow was observed. An infrared spectrum taken after 5 minutes reaction time indicated complete disappearance of the rhenium starting material and generation of an anion. After removal of the solvent *in vacuo*, the pale yellow, oily residue was extracted with water (10 ml). After filtration, the yellow solution was treated with excess aqueous Et_3OBF_4, which was added dropwise until the pH decreased to approximately 2. Addition of the ethylating agent was accompanied by cloudiness in the solution and precipitation of a pale yellow oil. Extraction from the aqueous solution with *n*-pentane (75 ml), removal of the solvent by rotary evaporation, and drying of the product *in vacuo* overnight resulted in the isolation of a yellow oil. Crystallization from *n*-heptane at -78° yielded as a white solid *cis*-$Ph_2MeGeRe(CO)_4C(OEt)Me$ (90 mg).

Reaction of $Ph_2GeMn(CO)_4COMe$ with (1) excess MeLi, (2) Et_3OBF_4

The features of this reaction are similar to those above. The complex $Ph_2GeMn(CO)_4COMe$ (0.65 g, 1.49 mmol) in diethyl ether (25 ml) was treated with excess 1.5 M MeLi in ether (5.5 ml, 8.25 mmol). The brown, oily residue, after solvent removal, was extracted with water (50 ml) and filtered to give a clear, yellow-orange solution. [Caution: water should be added to the brown oil slowly, since a vigorous reaction occurs with the excess methyllithium]. The dropwise addition of excess aqueous Et_3OBF_4 until a pH of about 2 was reached produced a yellow oil, which was extracted with *n*-pentane (150 ml). Removal of the solvent by rotary evaporation and drying *in vacuo* yielded the crude product *cis*-$Ph_2MeGeMn(CO)_4C(OEt)Me$ as a yellow oil (0.20 g). Attempts at crystallization from *n*-pentane and acetone-water yielded only oils. Slow sublimation (55°/0.01 mm) on to a water-cooled probe gave a yellow oil, whose infrared spectrum indicated partial decomposition of the *cis*-$Ph_2MeGeMn(CO)_4C(OEt)Me$ product to other carbonyl-containing compounds.

Reaction of $Ph_2GeMn(CO)_4COMe$ with (1) excess MeLi, (2) Et_4NCl

To $Ph_2GeMn(CO)_4COMe$ (1.20 g, 2.74 mmol) in diethyl ether (40 ml) was added 1.5 M MeLi (3.7 ml, 5.55 mmol), producing a brown solution. An infrared spectrum, recorded in ether after a few minutes, indicated complete reaction of the manganese starting material and formation primarily of *cis*-$Ph_2MeGeMn(CO)_4C(OLi)Me$, plus a little of the unidentified anion mentioned in the text. (Larger excesses of MeLi lead to the observation of only *cis*-$Ph_2MeGeMn(CO)_4C(OLi)Me$, as in the preceding reaction). Subsequent treatment in water (30 ml) with excess aqueous Et_4NCl (0.66 g, 4.0 mmol) produced a yellow-brown, oily precipitate. An attempt at crystallization from acetone-ether was unsuccessful. Extraction of the oil with ether (300 ml), reduction of the solution volume to 100 ml under reduced pressure, and cooling in the refrigerator yielded pale yellow crystals of [*cis*-$Ph_2MeGeMn(CO)_4C(O)Me$][Et_4N] (35 mg).

Reaction of [*cis*-$Ph_2MeGeMn(CO)_4C(O)Me$][Et_4N] with Et_3OBF_4

The ether extraction from the crude product in the preceding reaction left a large proportion of the product in

the brown, oily residue. This residue was dissolved in dichloromethane (30 ml), and treated with Et_3OBF_4. The progress of the reaction was monitored by infrared spectroscopy as small portions of the ethylating agent were added. Removal of the solvent by rotary evaporation, and extraction of the residue with *n*-pentane, gave a yellow solution. Solvent removal by rotary evaporation yielded an impure yellow oil, whose infrared and mass spectra identified it as *cis*-$Ph_2MeGeMn(CO)_4C(OEt)Me$.

Reaction of $Ph_2GeMn(CO)_4COMe$ with (1) deficit of MeLi, (2) Et_3OBF_4

A solution of the unidentified anion can be generated by the reaction of $Ph_2GeMn(CO)_4COMe$ with MeLi in ether in an approximately 2:1 mole ratio. For example, treatment of $Ph_2GeMn(CO)_4COMe$ (0.475 g, 0.95 mmol) with 1.5 M MeLi (0.30 ml, 0.45 mmol) gives a pale yellow solution containing an anionic intermediate which is <u>not</u> *cis*-$Ph_2MeGeMn(CO)_4C(OLi)Me$. (This behaviour can be contrasted with a reaction in which MeLi is in excess-*vide supra*). Removal of solvent and extraction with water leaves a residue of unreacted $Ph_2GeMn(CO)_4COMe$. Treatment of an aqueous solution of the unknown anion with excess aqueous Et_3OBF_4, until the pH is approximately 2, yields a yellow oil. Decantation of the

aqueous solution, washing with a small amount of water, and drying *in vacuo* yields a yellow oil, whose infrared and mass spectra identify it as impure *cis*-$Ph_2FGeMn(CO)_4C(OEt)Me$.

Reaction of $Ph_2GeMn(CO)_4COMe$ with (1) NaOMe, (2) Et_3OBF_4

To $Ph_2GeMn(CO)_4COMe$ (0.30 g, 0.69 mmol) in methanol (20 ml) was added sodium methoxide (0.038 g, 0.70 mmol). The solution was stirred for 19 hours. Removal of the solvent by rotary evaporation yielded a yellow oil, whose infrared spectrum in dichloromethane indicated an anionic material [ν(CO) 2040 (m), 1959 (s, sh), 1935 (vs)] as well as a little residual starting material. Extraction with water (15 ml), and filtration were followed by the dropwise addition of excess aqueous Et_3OBF_4, until the pH was approximately 2. A yellow oil was precipitated, and this was extracted with *n*-pentane (2 x 60 ml). The *n*-pentane extract was dried over anhydrous Na_2SO_4 overnight in the refrigerator. Filtration, and removal of the solvent by rotary evaporation, yielded a yellow oil. This was adsorbed on to alumina (*ca.* 2 g), and chromatographed on a column packed with alumina (50 g, 16 cm column height), using *n*-heptane as eluent. A single yellow fraction (*ca.* 50 ml) was collected, the volume reduced (to *ca.* 10 ml), and the solution cooled in the refrigerator. Colourless crystals of *cis*-$Ph_2FGeMn(CO)_4C(OEt)Me$ (45 mg) were obtained.

Reaction of $Ph_2GeMn(CO)_4COMe$ with (1) NaOMe, (2) Et_4NBr

The reaction of $Ph_2GeMn(CO)_4COMe$ with NaOMe in methanol was repeated, using excess NaOMe to avoid residual starting material. $Ph_2GeMn(CO)_4COMe$ (0.30 g, 0.69 mmol) and NaOMe (0.076 g, 1.4 mmol) were stirred in methanol (20 ml) for 24 hours. Subsequent treatment with excess aqueous Et_4NBr in water precipitated a pale yellow oil. The aqueous solution was decanted and the residue washed with water (20 ml). Drying *in vacuo* overnight, and crystallization from acetone-ether yielded pale yellow crystals of [*cis*-$Ph_2(HO)GeMn(CO)_4$-C(O)Me][Et_4N] (0.20 g).

CHAPTER V

The Synthesis of Non-Cyclic Carbene Complexes of Manganese and Rhenium, Containing Organo-germanium and -tin Ligands

Introduction

As described in Chapter I, transition metal carbene complexes have been widely studied over the past decade.[12-15] Metal carbonyl derivatives containing elements of the fourth main group, other than carbon, as ligands have also received much attention.[41-3] Not until 1970, however, were the first complexes prepared containing both carbene and group IV ligands, namely *trans*-$Ph_3M'Co(CO)_3C(OEt)Ph$ (M' = Sn, Pb).[51] Work by Dr. W. K. Dean in this laboratory has yielded carbene derivatives, notably of manganese, molybdenum and tungsten, containing group IV ligands,[52,53] and these have been referred to in the introduction to Chapter II. The novel cyclic germoxy- and stannoxy-carbene complexes, described in Chapter II, and their derivatives (see Chapter IV) can also be added to this class. Also, a number of manganese and rhenium carbene complexes, of a non-cyclic type, containing organo-germanium and -tin ligands have been prepared, and these new compounds are described below.

Synthesis and Characterisation of Complexes

The Synthesis of *cis*-$Ph_3GeMn(CO)_4C(OMe)Me$

The reaction of $Ph_3GeMn(CO)_5$ with methyllithium, followed by treatment of the resulting lithium acylate with Me_3OPF_6 or $MeOSO_2F$ in water, has been described earlier (Chapter II) as resulting in a mixture of *cis*-$Ph_3GeMn(CO)_4C(OMe)Me$ and a complex of empirical formula $Ph_2GeMn(CO)_4COMe$ (II-7). The former was the expected reaction product, and the latter has been found to belong to a novel class of heterocyclic carbene complexes, as described in Chapter II. The acylate intermediate has been isolated as a tetraethylammonium salt (II-5) and is well characterised (*vide infra*). In a reaction employing Me_3OPF_6 in the second step, a GLC analysis of the organic reaction product, which revealed it to be benzene (see Chapter II), has indicated that the Me_3OPF_6 acts as a protonating agent in the generation of $Ph_2GeMn(CO)_4COMe$, and it is assumed that $MeOSO_2F$ behaves similarly.

If either Me_3OPF_6 or $MeOSO_2F$ is used, the crude reaction product always contains predominantly $Ph_2GeMn(CO)_4COMe$. This can be observed in solution infrared spectra of the product. ^1H NMR spectroscopy allows the relative amounts of the two products to be determined using peak integrals. In one case where $MeOSO_2F$ was used a ratio of $Ph_2GeMn(CO)_4COMe$ to *cis*-$Ph_3GeMn(CO)_4C(OMe)Me$ of 3:1 was observed. In two cases where

Me_3OPF_6 was employed, ratios of 6:1 and 13:1 were found, showing that the reaction is somewhat unpredictable.

In one case, crystallization of a crude reaction mixture from acetone-water yielded yellow, needle-like crystals of *cis*-$Ph_3GeMn(CO)_4C(OMe)Me$ in low yield (4%). This material was not analytically pure but gave satisfactory solution infrared and mass spectra. In conjunction with the ^1H NMR spectra of crude reaction mixtures, the infrared and mass spectral results established the identity of the complex (see Tables XI and XII). The four-band infrared spectrum (also showing an extra shoulder, presumably due to the presence of more than one isomer in solution-*vide infra*) establishes the *cis*-geometry of the molecule. The mass spectrum shows the expected parent ion (m/e 530) and the stepwise loss of four carbonyl groups, thus resembling the spectra obtained for the ethoxycarbene complexes described below.

The Synthesis of Complexes of the Type *cis*-$R_3M'M(CO)_4C(OEt)R'$

As explained previously, the reaction of $Ph_3GeMn(CO)_5$ with methyllithium yields the lithium acylate *cis*-$Ph_3GeMn(CO)_4C(OLi)Me$. Subsequent treatment with aqueous Et_4NBr yields the salt [*cis*-$Ph_3GeMn(CO)_4C(O)Me$][Et_4N] (II-5), which has been well characterised by infrared and ^1H NMR spectroscopy, and microanalysis (see Tables XI-XIII). Although attempts at methylation of the lithium acylate yielded only

TABLE XI

CARBONYL STRETCHING FREQUENCIES, AND MASS SPECTRAL PARENT IONS FOR THE NON-CYCLIC CARBENE DERIVATIVES OF MANGANESE AND RHENIUM

Compound	Mass Spectral Parent Ion (m/e)[a]	Carbonyl Stretching Frequencies (cm^{-1})[b,c]			
cis-$Ph_3GeMn(CO)_4C(OEt)Me$	544	2056 (s)	1986 (s),	1967 (vs),	1962 (s, sh)
cis-$Ph_3SnMn(CO)_4C(OEt)Me$	590	2055 (s), 2051 (m, sh),	1986 (m),	1968 (vs),	1962 (s, sh)
cis-$Ph_3GeMn(CO)_4C(OEt)Ph$	606	2055 (s),	1983 (m),	1974 (vs),	1968 (s, sh)
cis-$Ph_3SnMn(CO)_4C(OEt)Ph$	652	2055 (s),	1983 (m),	1974 (vs),	1968 (s, sh)
cis-$Ph_3GeMn(CO)_4C(OMe)Me$	530	2057 (s), 2053 (m, sh),	1989 (m),	1970 (vs),	1962 (s, sh)
cis-$Me_3GeRe(CO)_4C(OEt)Me$	488	2065 (m),	1987 (s),	1967 (s),	1961 (s, sh), 1958 (vs)
[*cis*-$Ph_3GeMn(CO)_4C(O)Me$][Et_4N][d]	—	2023 (m),	1938 (vs),	1920 (s, sh),	1904 (s, sh)
cis-$Ph_3GeMn(CO)_4C(NHEt)Me$	543	2047 (m),	1981 (m, sh),	1976 (m),	1955 (vs), 1950 (s, sh)
cis-$Me_3GeRe(CO)_4C(NHEt)Me$	487	2058 (m),	1976 (s),	1951 (vs),	1945 (s, sh)

[a] Most abundant peak of isotope combination pattern of parent ion reported; isotope combination pattern of parent ion is as expected in all cases.

[b] *Cyclo*hexane solvent for all neutral complexes; dichloromethane for salt.

[c] Abbreviations as in Table I.

[d] $\nu(C\text{-}O^-)$ 1570 cm^{-1} (dichloromethane solution).

TABLE XII

^{1}H NMR DATA FOR THE NON-CYCLIC CARBENE DERIVATIVES OF MANGANESE AND RHENIUM

Compound	Chemical Shift (τ-value)[a,b] C-$\underline{CH}_3$[c]	Y-$\underline{CH}_2$-CH_3[d]	Y-CH_2-$\underline{CH}_3$[e]	Solvent
cis-$Ph_3GeMn(CO)_4C(OEt)Me$	7.55	6.21	8.64	$CDCl_3$
cis-$Ph_3SnMn(CO)_4C(OEt)Me$[f]	7.40	6.21	8.63	$CDCl_3$
cis-$Ph_3GeMn(CO)_4C(OEt)Ph$[g]	—	6.23	8.68	$CDCl_3$
cis-$Ph_3SnMn(CO)_4C(OEt)Ph$[g]	—	6.29	8.69	$CDCl_3$
cis-$Ph_3GeMn(CO)_4C(OMe)Me$[h]	7.58	—	—	$CDCl_3$
cis-$Me_3GeRe(CO)_4C(OEt)Me$[i]	7.24	5.53	8.42	CD_2Cl_2
[*cis*-$Ph_3GeMn(CO)_4C(O)Me$][Et_4N][j]	7.19	—	—	$(CD_3)_2CO$
cis-$Ph_3GeMn(CO)_4C(NHEt)Me$[k]				$CDCl_3$
Isomer 1	7.58[m]	6.30[o]	8.83	
Isomer 2	7.49[m]	7.06[p]	9.20	
cis-$Me_3GeRe(CO)_4C(NHEt)Me$[l]				$CDCl_3$
Isomer 1	7.21[n]	6.28[q]	8.60	
Isomer 2	7.35[n]	6.60[q]	8.64	

TABLE XII (continued)

[a]Relative to TMS at 10 τ. Peak integrals consistent with empirical formulae.

[b]Phenyl resonances complex multiplets at *ca.* 2.5-3.0 τ, except as noted.

[c]Singlet, except as noted.

[d]Quartet, except as noted. Y = O or N.

[e]Triplet. Y = O or N.

[f]$^4J_{(117,\ 119_{Sn}-1_H)}$ = 13.0 Hz.

[g]Resonances of phenyl group attached to carbene carbon atom split into two multiplets of intensity 3 and 2. The former coincides with the resonances of the other phenyl groups in the molecule. The latter is to higher field, appearing at τ 3.63 and 3.38, respectively, in the germanium and tin complexes.

[h]$O\text{-}C\underline{H}_3$ singlet at τ 6.27.

[i]$Ge\text{-}(C\underline{H}_3)_3$ singlet at τ 9.57.

[j]$N\text{-}C\underline{H}_2\text{-}CH_3$ quartet at τ 6.58; $N\text{-}CH_2\text{-}C\underline{H}_3$ triplet of triplets at τ 8.65

[k]$N\text{-}\underline{H}$ broad resonance at τ 2.05. Peak integral ratio for isomers 1:2 = *ca.* 3:4 for a crude sample of product. Almost all of isomer 1 removed by crystallization from *n*-hexane.

TABLE XII (continued)

[l]N-H broad resonance at τ 1.70, which did not disappear upon addition of D_2O to the $CDCl_3$ solution. Ge-($C\underline{H}_3$)$_3$ singlets at τ 9.61 and 9.63 for isomers 1 and 2, respectively. Peak integral ratio for isomers 1:2 = *ca.* 4:1 for crude sample of product.

[m]Appeared to be singlets, but peak expansions not obtained [see results for *cis*-$Me_3GeRe(CO)_4C(NHEt)Me$].

[n]Appeared to be singlets, but peak expansion revealed poorly resolved multiplets.

[o]Broad, unresolved signal.

[p]Pair of overlapping quartets.

[q]Appeared to be pair of overlapping quartets, but peak expansion also showed small, long range couplings. $^3J_{H\text{-}N\text{-}C\text{-}H}$ = 6.6 Hz (Isomer 1), 7.4 Hz (Isomer 2).

TABLE XIII

MELTING POINTS, YIELDS AND ANALYTICAL DATA FOR THE NON-CYCLIC CARBENE DERIVATIVES OF MANGANESE AND RHENIUM

Compound[a]	M.P.(°C)	% Yield	Calcd. % C	Calcd. % H	Found %[b] C	Found %[b] H
cis-$Ph_3GeMn(CO)_4C(OEt)Me$	107-8	88	57.51	4.27	57.33	4.42
cis-$Ph_3SnMn(CO)_4C(OEt)Me$	—[f]	29	53.01	3.94	52.93	4.00
cis-$Ph_3GeMn(CO)_4C(OEt)Ph$	112-4	86	61.54	4.16	61.62	4.34
cis-$Ph_3SnMn(CO)_4C(OEt)Ph$	130-2	3	57.18	3.87	57.18	3.86
cis-$Me_3GeRe(CO)_4C(OEt)Me$	—[g]	83	27.07	3.51	26.68	3.48
[*cis*-$Ph_3GeMn(CO)_4C(O)Me$][Et_4N][c]	dec. > 125	81	59.66	5.95	58.82	5.96
cis-$Ph_3GeMn(CO)_4C(NHEt)Me$[d]	—[f]	78[h]	57.62	4.46	57.05	4.58
cis-$Me_3GeRe(CO)_4C(NHEt)Me$[e]	—[g]	60	27.13	3.73	28.61	4.19

TABLE XIII (continued)

[a]All neutral compounds yellow; salt white.

[b]C, H analyses carried out in duplicate by the Microanalytical Laboratory of this Department (mean value given).

[c]% N calcd. 2.17; found 2.19.

[d]% N calcd. 2.58; found 2.77.

[e]% N calcd. 2.88; found 3.50.

[f]M.P. not reproducible; may reflect the presence of more than one isomer.

[g]Liquid at room temperature.

[h]Yield of analytically pure yellow oil. This compound reluctant to crystallize from *n*-hexane, and crystals obtained represent a yield of only *ca.* 6%.

small amounts of the expected methoxycarbene complex, it has been found that ethylation of the same acylate using Et_3OBF_4 proceeds cleanly to give the expected product, *cis*-$Ph_3GeMn(CO)_4C(OEt)Me$, in high yield (II-6). In analogous reactions a number of closely related derivatives have been prepared, containing organo-germanium and -tin ligands (V-1). These products have been well characterised by infrared, ^1H and ^{13}C NMR spectroscopy, and mass spec-

$$R_3M'M(CO)_5 + R'Li \xrightarrow{\text{ether}} cis\text{-}R_3M'M(CO)_4C(OLi)R' \xrightarrow[\text{water}]{Et_3OBF_4} cis\text{-}R_3M'M(CO)_4C(OEt)R' \qquad V\text{-}1$$

R = Ph, M' = Ge, Sn; M = Mn; R' = Me, Ph. R = Me; M' = Ge; M = Re; R' = Me.

trometry, and by microanalysis (see Tables XI-XIII). In the case of *cis*-$Ph_3GeMn(CO)_4C(OEt)R'$ (R' = Me, Ph), the products precipitated from the aqueous reaction mixtures were pure solids which had sharp melting points and gave good analytical data. The complex *cis*-$Ph_3SnMn(CO)_4C(OEt)Me$ was sometimes precipitated as a solid and sometimes as an oil, and oil formation was also observed in the case of *cis*-$Ph_3SnMn(CO)_4C(OEt)Ph$. In cases where oils were formed, the products were purified by chromatography. The complex *cis*-$Me_3GeRe(CO)_4C(OEt)Me$ is a liquid at room temperature and could also be purified by chromatography.

The fact that the complexes all possess *cis*-geometries at the central metal atom is clearly established by their

four-band solution infrared spectra in the carbonyl region (Table XI). This geometry supports the contention of Darensbourg and Darensbourg,[51] who have suggested that, in a given molecule, the carbonyl group of highest force constant is most susceptible to attack by organolithium reagents. This point has been previously discussed in Chapter II. The existence of extra shoulders in the solution infrared spectra of *cis*-$Ph_3SnMn(CO)_4C(OEt)Me$ and *cis*-$Me_3GeRe(CO)_4C(OEt)Me$ (see Table XI and Figure 20) probably arises from hindered rotation about the carbene carbon to oxygen bond, which can lead to two isomers.[66] The existence of two isomers in the case of *cis*-$Me_3GeRe(CO)_4C(OEt)Me$ has also been indicated by a variable temperature ^1H NMR study (*vide infra*).

The suggested formulations of the complexes are fully supported by mass spectral results (Table XI). In each case a parent ion with the expected isotope combination pattern is observed. For the complexes *cis*-$R_3M'M(CO)_4C(OEt)R'$ (where R = Ph; M' = Ge, Sn; M = Mn; R' = Me, Ph), the stepwise loss of four carbonyl groups from the parent ion is observed in each case. For the trimethylgermyl- complex, *cis*-$Me_3GeRe(CO)_4C(OEt)Me$, however, competing losses of methyl and carbonyl groups from the parent ion are observed.

The formulations of the new compounds are further confirmed by ^1H NMR results. The data from spectra recorded at ambient temperatures are reported in Table XII, and the spectrum of *cis*-$Ph_3GeMn(CO)_4C(OEt)Me$ is shown in Figure 21.

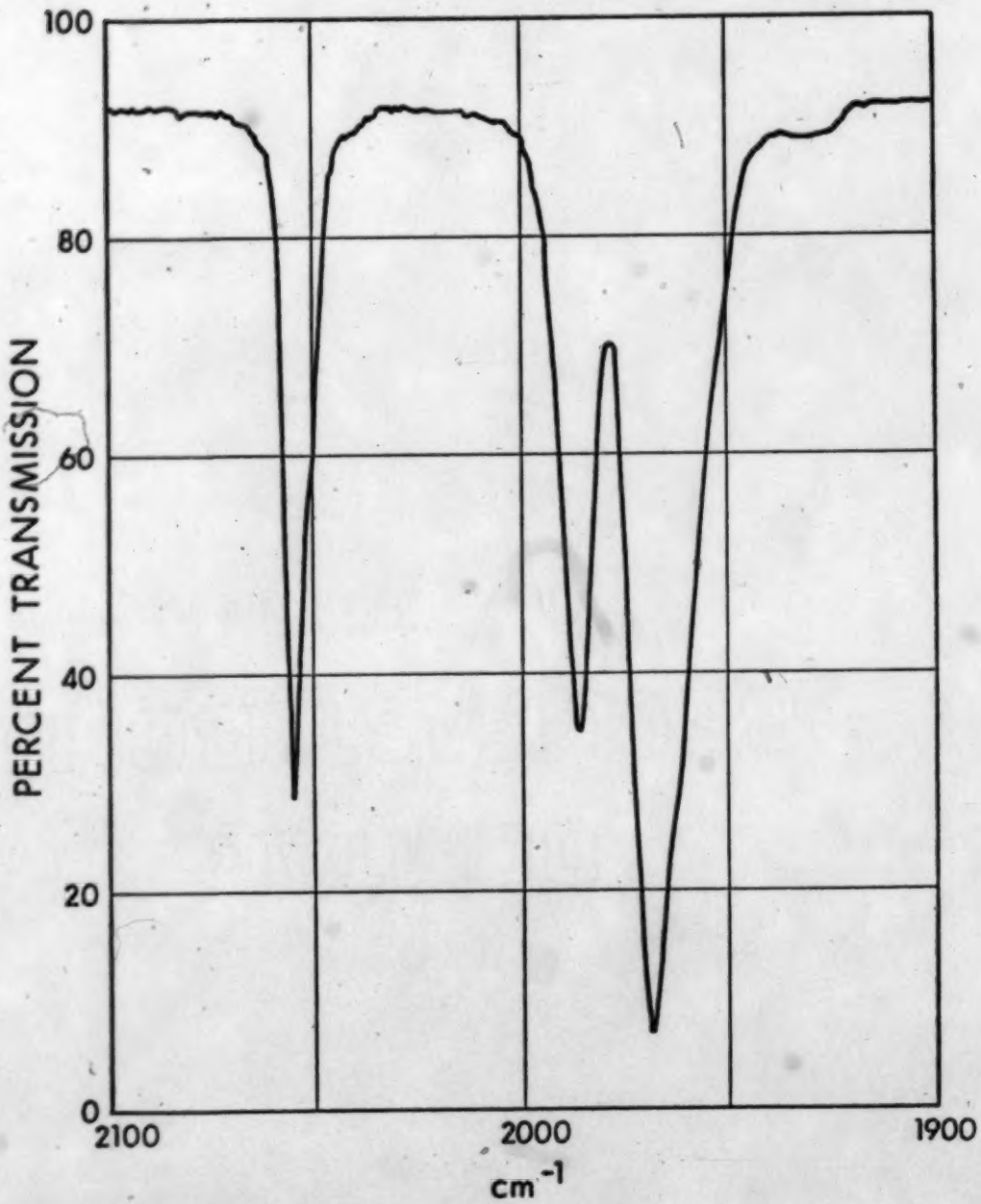


Figure 20. Infrared spectrum [ν(CO) region] of *cis*-$Ph_3SnMn(CO)_4C(OEt)Me$ in *cyclo*hexane.

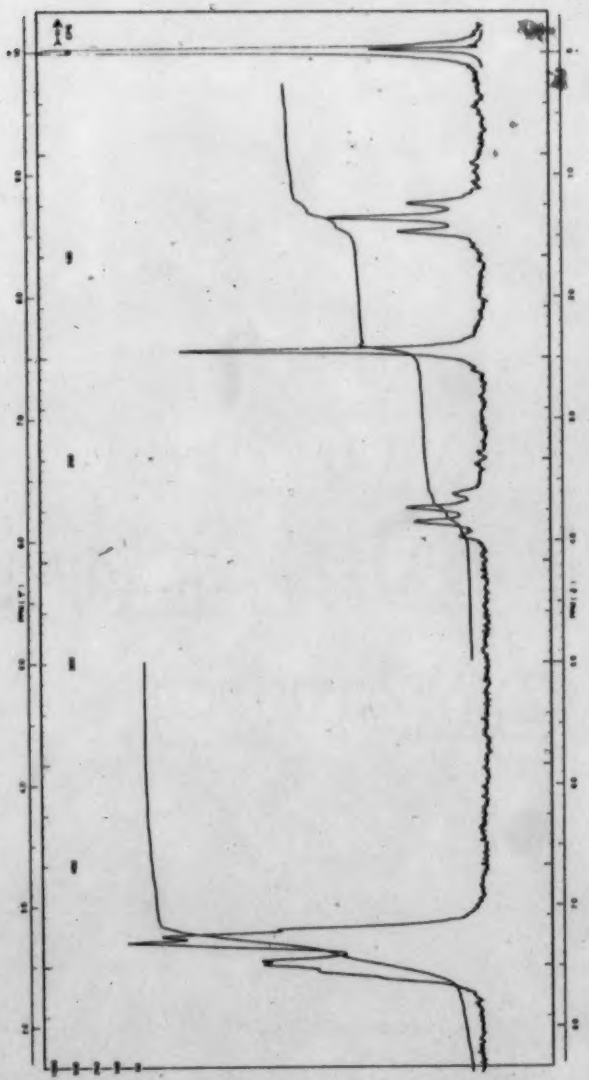


Figure 21. ^1H NMR spectrum of *cis*-$Ph_3GeMn(CO)_4C(OEt)Me$ in $CDCl_3$.

A more detailed ^1H NMR study of the complex *cis*-$Me_3GeRe(CO)_4$-C(OEt)Me has also been carried out. The sharp signals which are observed at ambient temperature in CD_2Cl_2 broaden as the temperature is lowered and at -50°C fairly sharp signals due to two distinct species are observed. These changes are completely reversible. A closer examination of the C-$C\underline{H}_3$ resonance alone, using scale expansion, revealed that at -60°C a limiting low temperature situation was reached, showing two sharp singlets of approximately equal intensity separated by 15.0 Hz. As the temperature is raised, peak broadening is observed, and the peaks coalesce (coalescence temperature -33°C). The single, averaged signal then continues to sharpen up to +10°C when a limiting situation is reached. A detailed line-shape analysis has not been carried out. A variable concentration study, again of the expanded C-$C\underline{H}_3$ region, carried out at -40°C, established that the process is concentration-independent, and this behaviour can therefore be contrasted with the concentration-dependent dimer-monomer equilibrium discussed in Chapter III. It seems likely that the isomerism observed for *cis*-$Me_3GeRe(CO)_4C(OEt)Me$ involves hindered rotation about the carbene carbon to oxygen bond. A process of this type has been studied by variable temperature ^1H NMR in the case of $Cr(CO)_5C(OMe)Me$, using a similar temperature range[66] (the limiting low temperature situation was reached at -40°C). The possibility that, in

the case of *cis*-$Me_3GeRe(CO)_4C(OEt)Me$, hindered rotation about the metal to carbene carbon bond causes the observed spectral changes cannot, however, be eliminated on the basis of existing information.

The fact that the novel compounds described here are in fact carbene complexes has been confirmed by a ^{13}C NMR spectrum of *cis*-$Me_3GeRe(CO)_4C(OEt)Me$, carried out at ambient temperature in $CDCl_3$, which revealed a signal at -314.8 p.p.m., a chemical shift indicative of a carbene carbon atom attached to a third-row transition metal. For comparison purposes, that in $W(CO)_5C(OEt)Me$ occurs at -330.1 p.p.m.[21] Further details of this ^{13}C NMR spectrum will be discussed in Chapter VI.

The Synthesis of Ethylaminocarbene Complexes

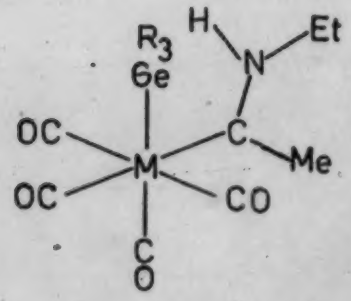
The reactivity of alkoxycarbene complexes towards primary or secondary amines to yield amminocarbene complexes has been well established. One such example was referred to in I-2.[26] Thiocarbene complexes can be similarly generated by reacting alkoxycarbene complexes with thiols (see for example I-3[12]). It has been found that no reaction occurs when *cis*-$Ph_3GeMn(CO)_4C(OEt)Me$ is stirred with excess, neat ethanethiol in a pressure bottle for 24 hours. Treatment of this complex or *cis*-$Me_3GeRe(CO)_4C(OEt)Me$ with ethylamine in a similar manner, however, yields the expected ethylamino derivatives

cis-$Ph_3GeMn(CO)_4C(NHEt)Me$ and *cis*-$Me_3GeRe(CO)_4C(NHEt)Me$. ^1H NMR spectra suggest that both of these complexes exist as a mixture of two isomers at room temperature (*vide infra*).

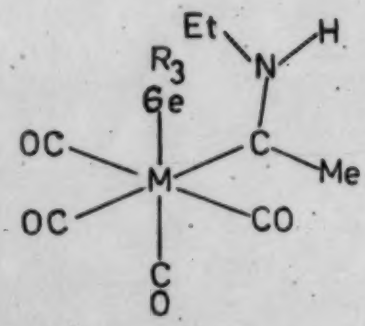
Solution infrared spectra of the two new aminocarbene derivatives confirm their *cis*-stereochemistry at the central metal atom (Table XI). The suggested formulations are supported by mass spectra, which reveal the expected parent ion in each case (Table XI). In the case of *cis*-$Ph_3GeMn(CO)_4C(NHEt)Me$, the stepwise loss of four carbonyl groups from the parent ion is observed. In the spectrum of *cis*-$Me_3GeRe(CO)_4C(NHEt)Me$, competing losses of methyl and carbonyl groups are seen, with the former apparently favoured. Analytical results for the new complexes are presented in Table XIII.

^1H NMR spectra, recorded at ambient temperatures, have shown that in $CDCl_3$ solutions of either *cis*-$Ph_3GeMn(CO)_4C(NHEt)Me$ or *cis*-$Me_3GeRe(CO)_4C(NHEt)Me$ two species exist. Furthermore, a variable temperature study of the rhenium complex, in toluene-d_8, revealed no spectral changes up to a temperature of 110°C., establishing that the two species present do not interconvert rapidly on the NMR time scale. The ^1H NMR spectrum of a sample of the manganese derivative after crystallization from *n*-hexane revealed that one species had been almost entirely removed, implying that the two species do not interconvert under normal conditions. It has

been shown earlier that there is a high barrier to rotation about carbene carbon to nitrogen bonds in aminocarbene complexes.[70] It has been found, for example, that $Cr(CO)_5$-C(NHMe)Me was formed as a *cis*-isomer[71] (that is, the two methyl groups were *cis* to each other with respect to the carbene carbon to nitrogen bond). This could not be converted to the *trans*-isomer thermally, but only by base catalysis.[72] Therefore, it seems highly likely that the two species present in solutions of both of the novel aminocarbene complexes, described herein, arise from isomerism about the carbene carbon to nitrogen bond. The two isomers are shown in 23 and 24. It must be assumed that the two



23



24

R = Ph, M = Mn; R = Me, M = Re.

isomers have degenerate carbonyl stretching bands in the case of the rhenium complex, which shows a simple four band solution infrared spectrum. In the manganese case, however, an extra shoulder indicates that more than one species is present (see Table XI).

EXPERIMENTAL

All reactions were carried out at ambient temperature under a static nitrogen atmosphere and products were handled with minimum exposure to air. Diethyl ether and hydrocarbon solvents were dried by distillation from calcium hydride and solvents were saturated with nitrogen prior to use.

The compounds $Ph_3GeMn(CO)_5$, $Ph_3SnMn(CO)_5$, and $Me_3GeRe(CO)_5$ were prepared as described in Chapter II. The methylating agents Me_3OPF_6 and $MeOSO_2F$ were purchased from Aldrich Chemical Company, Inc., Milwaukee, Wis. Ethylamine and ethanethiol were obtained from BDH Chemicals Limited, Poole, England. Other reagents and materials were obtained from sources cited in Chapters II and IV.

Melting points, and solution infrared and mass spectra were obtained as described in Chapter II. Microanalyses were performed in the Microanalytical Laboratory of this Department. ^1H NMR spectra were recorded as described in Chapter II, except for the variable temperature study of *cis*-$Me_3GeRe(CO)_4C(NHEt)Me$ which was carried out using a Perkin-Elmer R-32 instrument, operating at 90 MHz.

Preparation of *cis*-$Ph_3GeMn(CO)_4C(OMe)Me$

The procedure is very similar to that used in the synthesis of the cyclic carbene complexes prepared in Chapter II. Treatment of $Ph_3GeMn(CO)_5$ (0.50 g, 1.0 mmol) with a slight excess of methyllithium in ether rapidly generates the lithium acylate, *cis*-$Ph_3GeMn(CO)_4C(OLi)Me$. Subsequent treatment of an aqueous solution of this acylate with either Me_3OPF_6 (excess aqueous solution added until the pH ~ 2) or $MeOSO_2F$ (0.1 ml added from a syringe, which produces a final pH ~ 3) rapidly yields a white or pale yellow powder, which contains a mixture of *cis*-$Ph_3GeMn(CO)_4C(OMe)Me$ and $Ph_2GeMn(CO)_4COMe$ with the latter always predominating. In one instance where $MeOSO_2F$ was used, the precipitate was recrystallized from acetone-water, yielding yellow, needle-like crystals of analytically impure *cis*-$Ph_3GeMn(CO)_4C(OMe)Me$ (20 mg). It has more recently been established that the complexes whose syntheses are described below are stable towards column chromatography on alumina, and this may prove to be the preferred method of isolation of larger amounts of *cis*-$Ph_3GeMn(CO)_4C(OMe)Me$.

Preparation of Ethoxycarbene Complexes

The method is essentially the same as that described above. Treatment of $Ph_3GeMn(CO)_5$, $Ph_3SnMn(CO)_5$, or $Me_3GeRe(CO)_5$ with a slight excess of methyllithium in ether

gives a rapid reaction, and is accompanied by a colour change from colourless to yellow. After a few minutes, the infrared spectrum of the carbonyl region, recorded in diethyl ether, shows four bands due to the *cis*-disubstituted lithium acylate. Subsequent ethylation of the lithium acylate in water, using excess aqueous Et_3OBF_4, which is added dropwise until the pH is approximately 2, yields the product. In some cases the product precipitates as a pure solid, in others as an oil (see text). In the latter case the product can be purified by column chromatography on alumina, using *n*-heptane or *n*-hexane as eluent, followed by crystallization of the product from a hydrocarbon solution. An attempt to crystallize *cis*-$Me_3GeRe(CO)_4C(OEt)Me$ from *n*-pentane at -78°C was successful, but the pale yellow crystals melted below room temperature. In the case of *cis*-$Ph_3SnMn(CO)_4C(OEt)Ph$ an attempt was made to crystallize the material without prior chromatography. The solid obtained was rather impure, and, was then chromatographed and recrystallized to obtain a pure sample of the product. It is thought that, if the crude oil were initially chromatographed and then crystallized once, the yield of pure product could be increased somewhat over that reported in Table XIII.

Preparation of Ethylaminocarbene Complexes

cis-$Ph_3GeMn(CO)_4C(OEt)Me$ (0.40 g, 0.74 mmol) was added to ethylamine (*ca.* 20 ml) in a pressure bottle. After capping the bottle, the solution was magnetically stirred for 4.5 hours. The bottle was opened, and the excess ethylamine was evaporated under a stream of nitrogen. The yellow, oily residue was extracted with *n*-pentane (150 ml), and the solvent removed by rotary evaporation to give *cis*-$Ph_3GeMn(CO)_4C(NHEt)Me$ as a yellow oil (0.31 g). This compound was reluctant to crystallize from *n*-hexane and only low yields (*ca.* 25 mg) of poor quality crystals have been obtained.

The compound *cis*-$Me_3GeRe(CO)_4C(NHEt)Me$ can be prepared in an analogous fashion from *cis*-$Me_3GeRe(CO)_4C(OEt)Me$. The aminocarbene complex can be chromatographed on alumina using *n*-heptane as eluent, and sublimes at 60°C/0.01 mm onto a probe cooled to -78° to give a yellow solid. The compound melts, however, as the probe warms to room temperature.

CHAPTER VI

Carbon-13 NMR Spectra of Carbene Complexes of Manganese and Rhenium, and of a Compound Containing a Ketonic Oxygen Atom Coordinated to Rhenium

Introduction

Over the past several years the quantity of ^{13}C NMR data for transition metal carbonyl complexes has increased rapidly. A comprehensive review by Todd and Wilkinson[73] is a useful guide to the results published to date and the conclusions drawn therefrom. The nuclei ^{55}Mn, ^{185}Re and ^{187}Re, all with I = 5/2, possess quadrupole moments which can potentially broaden the signals of carbon atoms bound directly to them, and it is clear that carbonyl derivatives of manganese and rhenium have so far received little attention.[73]

In keeping with the highly electrophilic nature of carbene carbon atoms bound to transition metals, their resonances in ^{13}C NMR spectra appear at very low field. Spectra of many carbene complexes, a large number of them also containing carbonyl groups,[73] have been obtained. Studies to date, however, have dealt mainly with carbene complexes of chromium and tungsten,[21,74,75] of which a large number exist. The data presented herein fully

support the formulation of the novel cyclic complexes described in Chapter II as metal carbenes, and represent the first ^{13}C NMR results for carbene complexes of manganese and rhenium.

In Chapter II, the question of the most appropriate representation of the structure of the new complexes was discussed in terms of the potential canonical forms 16 and 17. While 17, the carbene formulation, appears appropriate on the basis of existing evidence, there is no precedent in the literature on which to base a prediction of the chemical shift of the acyl carbon atom in a structure of the type 16. Acyl carbon resonances in metal acyls appear at *ca.* -250 p.p.m. (see Chapter VII) and the effect of coordination of the oxygen atom to germanium or tin, as in 16, cannot be estimated. A ^{13}C NMR study of adducts involving ketonic oxygen atoms and main group metals such as zinc and aluminum, of which a number exist,[76] may prove informative in this regard. Further examination of the literature indicated that a number of carbonyl complexes containing ketonic oxygen atoms coordinated to transition metals have been prepared, and that none of these have been examined using ^{13}C NMR. In view of the fact that, in some cases, interesting structural alternatives have been mentioned (*vide infra*), the ^{13}C NMR spectrum of a complex containing a ketonic oxygen atom bound to rhenium has been recorded, as the first step in a study of such complexes.

Results and Discussion

^{13}C NMR Results for Carbene Complexes of Manganese and Rhenium

The ^{13}C NMR results are summarized in Table XIV, and several points are worthy of discussion. The spectrum of $Me_2GeMn(CO)_4COMe$ at ambient temperature, under conditions where the monomeric form of the complex predominates, reveals a resonance at -338.0 p.p.m., a region generally associated with carbene carbon resonances in metal carbene complexes. By way of comparison, the complex $Cr(CO)_5C(OEt)Me$ exhibits a carbene carbon resonance at -357.3 p.p.m.[21] The low temperature spectrum of $Me_2GeMn(CO)_4COMe$, under conditions where both monomeric and dimeric forms are present in substantial amounts , reveals two peaks at -335.0 and -337.6 p.p.m., which can be assigned to their carbene carbon atoms.

Further support for the carbene formulations of the molecules comes from a spectrum of $Me_2GeRe(CO)_4COMe$ (see Figure 22), recorded under conditions where the dimeric form predominates, which shows a peak at -305.7 p.p.m. This value agrees closely with that of a carbene complex of a more conventional type, *cis*-$Me_3GeRe(CO)_4C(OEt)Me$, for which a value of -314.8 p.p.m. was obtained. The fairly large shift to higher field (*ca.* 30 p.p.m.) of the carbene

TABLE XIV

^{13}C NMR DATA FOR CARBENE COMPLEXES OF MANGANESE AND RHENIUM

Compound	Chemical Shift [a]			
	C (carbene)	C-$\underline{C}H_3$	Ge-$\underline{C}H_3$	$\underline{C}O$
$Me_2GeMn(CO)_4COMe$ [b]	-338.0	-49.2	- 9.5	-216.5 [f]
$Me_2GeMn(CO)_4COMe$ [c]	-337.6	-50.8	- 9.5	-216.4
$[Me_2GeMn(CO)_4COMe]_2$ [c]	-335.0	-49.9	-13.4	-216.4
$[Me_2GeRe(CO)_4COMe]_2$ [d]	-305.7	-53.9	-13.8	-191.8 [g]
				-190.5
				-190.0
				-188.8
cis-$Me_3GeRe(CO)_4C(OEt)Me$ [d,e]	-314.8	-50.0	- 4.5	-194.6 [h]
				-192.5
				-190.2

[a] Chemical shifts in p.p.m. relative to tetramethylsilane; $CDCl_3$ solvent.

[b] Determined at 35°C

[c] Determined at -30°C. Mixture of monomer and dimer present. Assignment of peaks to monomer and dimer tentative (based in part on peak intensities).

[d] Determined at 45°C.

[e] O-$\underline{C}H_2$-CH_3 -76.8; O-$CH_2\underline{C}H_3$ -14.4. O-$\underline{C}H_2CH_3$ signal overlaps with centre of $CDCl_3$ triplet. Therefore, lowest field peak of $CDCl_3$ triplet used as internal standard (-78.30 p.p.m. from TMS).

[f] Line width *ca.* 150 Hz.

[g] Line width *ca.* 12 Hz. Peak intensities for $\underline{C}O$ resonances not equal (may be affected by presence of small amounts of monomer).

[h] Line width *ca.* 25 Hz. Relative peak intensities for $\underline{C}O$ resonances of 2:1:1 (lowest field peak of intensity 2).

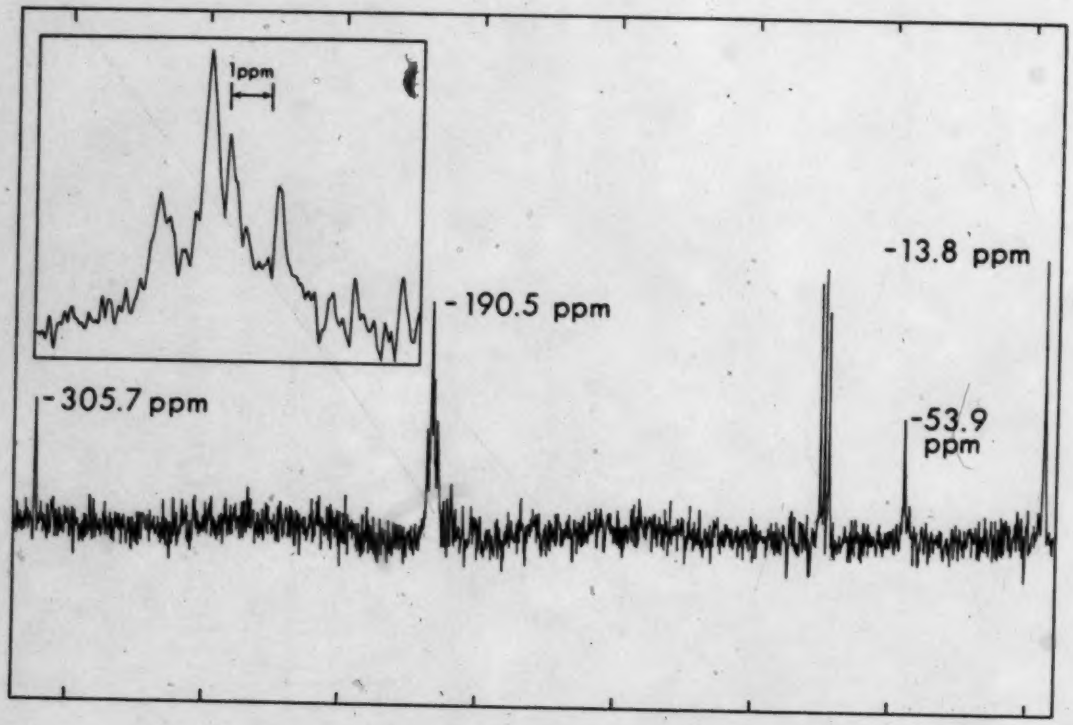


Figure 22. ^{13}C NMR spectrum of $[Me_2GeRe(CO)_4COMe]_2$ in $CDCl_3$ (including an expansion of the carbonyl region).

carbon resonances on going from manganese to rhenium is consistent with a shift of similar magnitude on going from carbene complexes of chromium to their tungsten analogs.[21]

The carbonyl carbon resonances of the manganese complexes appear as broad, unresolved peaks, consistent with earlier results for manganese carbonyl complexes.[73] In the rhenium case quadrupole broadening is less severe and the carbonyl peaks are clearly resolved. The improved resolution of carbonyl carbon atoms bound to rhenium, compared with manganese complexes, is supported by the results in Chapter VII. The observed shift of carbonyl resonances to higher field by *ca.* 25 p.p.m. on going from manganese to rhenium, parallels a change of similar magnitude when comparing chromium and tungsten carbonyl complexes, respectively.

^{13}C NMR Results for a Compound Containing a Ketonic Oxygen Atom Coordinated to Rhenium

The ^{13}C NMR spectrum of the complex 25, first prepared by Kaesz *et al.*,[77] is shown in Figure 23. The data are summarized in Table XV. The observation of three resonances, of relative intensities 2:1:1, for the carbon monoxide ligands implies that the chelating group is planar, unless accidental degeneracy is involved. The assignment of the ketonic carbon resonance has been confirmed using a sample

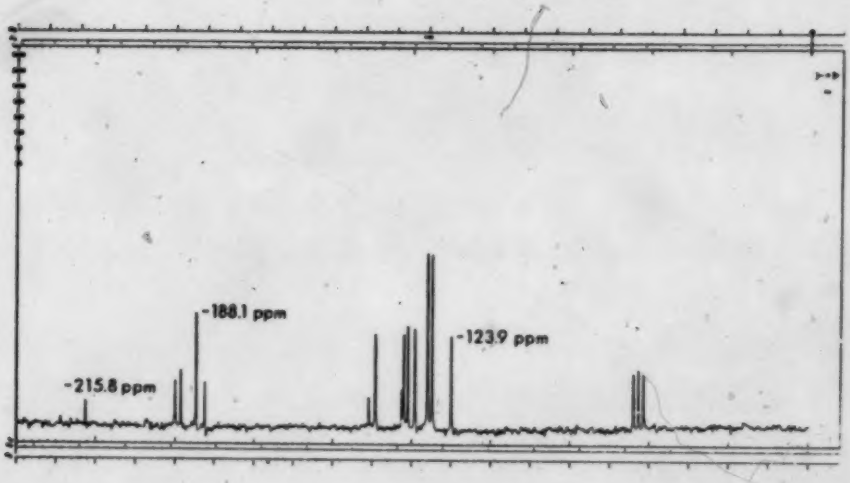


Figure 23

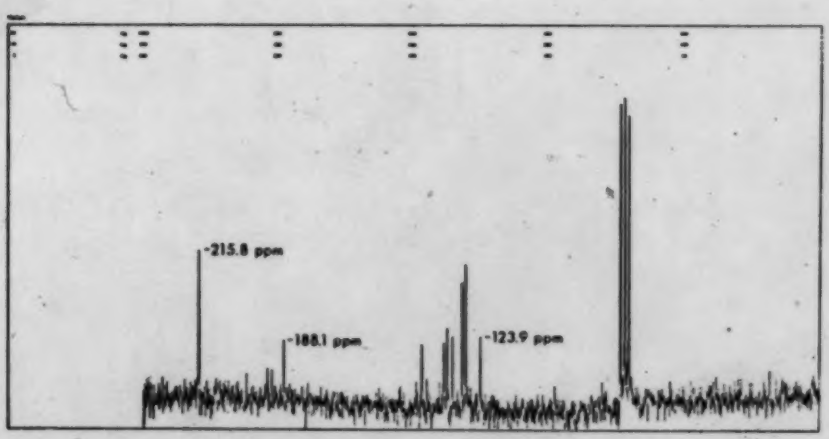


Figure 24

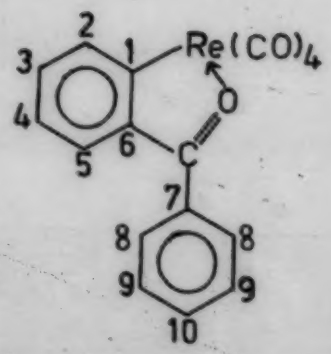
Figure 23. ^{13}C NMR spectrum, in $CDCl_3$, of the complex containing a ketonic oxygen atom coordinated to rhenium.

Figure 24. ^{13}C NMR spectrum, in $CDCl_3$, of a ^{13}C enriched sample of the complex containing a ketonic oxygen atom coordinated to rhenium.

TABLE XV

^{13}C NMR DATA FOR THE COMPOUND CONTAINING A KETONIC OXYGEN ATOM COORDINATED TO RHENIUM[a]

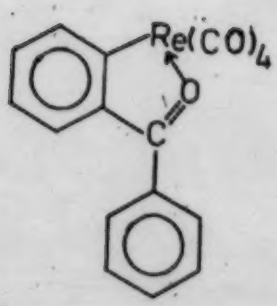
Chemical Shift	Assignment[b]
-215.8	C=O
-193.5	
-192.0	C≡O[c]
-188.1	
-185.9	1, 6, or 7
-144.7	1, 6, or 7
-142.9	2, 3, 4, 5, or 10
-136.4	1, 6, or 7
-135.8	2, 3, 4, 5, or 10
-134.8	2, 3, 4, 5, or 10
-133.0	2, 3, 4, 5, or 10
-129.8	8, or 9
-128.7	8, or 9
-123.9	2, 3, 4, 5, or 10



[a]Chemical shifts in p.p.m. relative to tetramethylsilane; $CDCl_3$ solvent; spectrum recorded at 45°C.

[b]Assignment of phenyl resonances based on relative peak intensities in proton-decoupled spectrum.

[c]Relative peak intensities of carbonyl resonances 2:1:1. (Peak at highest field of intensity 2).



25

of the complex *ca.* 10% enriched with ^{13}C at the ketone position (see Figure 24). The ketonic carbon resonance appears at -215.8 p.p.m. and is shifted to lower field by 19.4 p.p.m. relative to the ketonic carbon resonance in benzophenone. All chemical shift values were determined in $CDCl_3$ solutions.

Another noteworthy feature of the spectrum of 25 involves the phenyl carbon resonances. The signal due to one of the phenyl carbon atoms is highly deshielded compared with the other phenyl resonances, appearing in the carbonyl region at -185.9 p.p.m. This was discovered in a proton-coupled experiment in which this resonance broadened while the three carbonyl resonances remained sharp. This experiment also indicated that the phenyl carbon atom in question was not bound to a hydrogen atom, since it merely

broadened rather than splitting into a widely spaced doublet. This assignment agreed with that based on relative peak intensities of the phenyl carbons in proton-decoupled spectra. The three weakest signals of the phenyl resonances should be due to carbon atoms not bound to hydrogen, and therefore unable to benefit from Overhauser enhancement. The peak at -185.9 p.p.m. is one of these three. It is not known which of the three possible phenyl carbon atoms in 25 gives the resonance at - 185.9 p.p.m., and no clue can be gained from related complexes. The phenyl carbon atom bound to rhenium in $PhRe(CO)_5$ appears in the normal phenyl region (see Chapter VII), and the phenyl resonances in benzophenone are closely grouped between -137.6 and -128.1 p.p.m.

A number of complexes related to 25 exist, in which ketonic oxygen atoms are coordinated to manganese[77-81] and iridium,[78] and such complexes may be sources of further data. Potential applications of this type of study include structural elucidation in molecules formulated as having several possible resonance forms, one of them containing a coordinated ketonic oxygen atom.[82,83] Also some controversy surrounds complexes of the type 18, briefly discussed in Chapter II, since X-ray structural data does not distinguish possibilities involving bridging carbene or ketonic groups between two metal atoms.[59] An attempt at obtaining the ^{13}C NMR spectrum of the dimethyl analog of

18 was unsuccessful and this molecule appears to be rather unstable in solution. More stable complexes in which the same structural possibilities exist have recently been prepared however.[84,85] A crystal structure of one of these has been completed, but fails to distinguish between possibilities involving bridging carbene and ketonic groups.[86]

EXPERIMENTAL

The compounds $Me_2GeMn(CO)_4COMe$ and $Me_2GeRe(CO)_4COMe$ were prepared as described in Chapter II. The complex *cis*-$Me_3GeRe(CO)_4C(OEt)Me$ was prepared as in Chapter V. The rhenium complex, 25, was prepared by the method of Kaesz *et al.*[77] from $MeRe(CO)_5$ and benzophenone in toluene. The compound $MeRe(CO)_5$ was prepared by the method of Hieber *et al.*[87] Benzophenone was purchased from Fischer Scientific Company, Fair Lawn, N.J. Benzophenone, 90% ^{13}C enriched at the ketone carbon atom, was purchased from Merck, Sharp and Dohme, Canada, Ltd., Kirkland, Que., and was diluted to a level of *ca.* 10% ^{13}C enrichment before preparation of an enriched sample of the rhenium complex. Toluene was dried by distillation from sodium prior to use.

^{13}C NMR spectra were recorded using the Fourier transform pulsed NMR technique. Proton-decoupling was employed except as noted in the discussion. Varian HA-100 and Bruker HFX-90 spectrometers were used, operating at 25.15 MHz and 22.6 MHz, respectively. The number of scans was typically 10,000 to 20,000 for the carbene complexes, and 4,000 for the compound of Kaesz *et al.*; the delay between scans was of the order of 0.4 to 0.8 seconds; the flip angle was approximately 45°. All spectra were recorded in $CDCl_3$ and no relaxation agent was used in any instance. ^{13}C

chemical shifts were measured relative to the centre of the $CDCl_3$ triplet (except as noted in Table XIV) and are reported relative to TMS by use of the relation $\delta(TMS) = \delta(CDCl_3) - 77.035$ p.p.m. The sign convention employed gave carbon atoms deshielded with respect to TMS negative δ values. In cases where several spectra of a particular complex were obtained, chemical shifts were reproducible to ±0.1 p.p.m. Solution concentrations were *ca.* 1 M and 0.5 M for $Me_2GeMn(CO)_4COMe$ at +35° and -30°C respectively; *ca.* 0.5 M for $[Me_2GeRe(CO)_4COMe]_2$; *ca.* 1 M for *cis*-$Me_3GeRe(CO)_4C(OEt)Me$; *ca.* 0.5 M for the compound of Kaesz and 0.05 M for a 10% ^{13}C enriched sample of the same complex.

CHAPTER VII

A Carbon-13 NMR Study of Some Pentacarbonylrhenium Complexes

Introduction

The nuclei ^{55}Mn, ^{185}Re and ^{187}Re, all with I = 5/2, possess quadrupole moments which can potentially broaden the signals of carbon atoms bound directly to them. Carbonyl carbon resonances in manganese carbonyl derivatives are typically broad[73] (see Chapter VI) and, possibly because of expectations of similar behaviour in the case of rhenium, only two rhenium carbonyl complexes have been investigated prior to this work, namely $Re_2(CO)_{10}$ and $BrRe(CO)_5$. These compounds were recently reported by Todd and Wilkinson[88] to give "fairly well resolved" spectra at ambient temperatures in THF. These authors have also demonstrated that resonances broadened by coupling to quadrupolar transition metal nuclei can be significantly sharpened by sufficiently cooling the samples.[88]

In earlier work with carbene derivatives of manganese and rhenium, ^{13}C NMR proved to be a valuable tool in assigning structures to these complexes (see Chapters II and VI). In view of the high quality of spectra obtained for the rhenium complexes (described in Chapter VI), we have studied a wider range of rhenium carbonyl derivatives.

In this Chapter are presented results for an extensive series of neutral mono-substituted rhenium pentacarbonyl complexes, $XRe(CO)_5$, plus one derivative of the type $[LRe(CO)_5][PF_6]$ ($L = CH_3CN$).* Most of the neutral complexes gave sharply resolved spectra at ambient temperatures in $CDCl_3$, and an excellent spectrum of the salt was obtained at ambient temperature in CD_3CN. In the case of two neutral derivatives studied at high temperatures in toluene-d_8, resonances due to inequivalent carbonyl carbon atoms were still clearly resolvable at 100°C. The ^{13}C NMR chemical shifts are discussed in terms of their correlation with Cotton-Kraihanzel(CK) carbonyl stretching force constants and the limitations of this often-used treatment are pointed out.

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*In this discussion of these rhenium derivatives and related complexes, the symbol L will refer to neutral two-electron donor ligands such as phosphines or acetonitrile and X will refer to ligands which may formally be described as neutral one-electron donors or anionic two-electron donors, e.g., $(CH_3)_3Si$, Br, CH_3.

Results and Discussion

Neutral Complexes of the Type $XRe(CO)_5$

Recently it has been shown that ^{13}C NMR spectra of carbonyl derivatives of transition metals with nuclear quadrupole moments can be obtained by the method of "temperature relaxation."[88] In the studies of rhenium carbonyl derivatives, described herein, it has been found that quadrupole broadening is not a problem in most cases. Satisfactory spectra can usually be obtained at ambient temperatures in $CDCl_3$ (see Table XVI). Difficulties have been encountered only with $Re_2(CO)_{10}$, which gave one broad signal at *ca.* -191.2 p.p.m. relative to TMS, presumably due to the eight equivalent equatorial carbonyl carbon atoms, and $(CH_3)_3PbRe(CO)_5$ for which a broad, unresolved signal in the carbonyl region at *ca.* -189.3 p.p.m. was observed. In the case of $ClRe(CO)_5$ there were severe solubility limitations in $CDCl_3$ and after several thousand pulses no carbonyl resonances were observed.

The ^{13}C NMR results will now be discussed under two headings:

(a) resonances due to carbon atoms other than carbonyl carbon atoms, and

(b) resonances due to carbonyl carbon atoms.

TABLE XVI

^{13}C NMR DATA FOR PENTACARBONLYRHENIUM COMPLEXES[a]

Compound	δCO(*cis*)	δCO(*trans*)	Line width[b]	Other δ (assignment) [coupling constants]
$Cl_3SiRe(CO)_5$	-180.5	-178.5	11	
$(CH_3)_3SiRe(CO)_5$	-187.9	-182.9	9	-6.6 (CH_3)
$(CH_3)_3GeRe(CO)_5$	-187.5	-182.7	10	-4.9 (CH_3)
$(CH_3)_3SnRe(CO)_5$	-187.7	-182.9	13	+7.5 (CH_3); [$^1J(^{117}Sn-^{13}C)$ = 241 Hz; $^1J(^{119}Sn-^{13}C)$ = 252 Hz]
$(CH_3)_3PbRe(CO)_5$	----- *ca.* -189.3[c] -----			+5.0 (CH_3); [$^1J(^{207}Pb-^{13}C)$ = 88 Hz]
$CH_3Re(CO)_5$	-185.2	-181.3	8	+38.0 (CH_3)
$C_6H_5Re(CO)_5$	-183.6	-181.7	4	-145.5 (*o*- or *m*-); -134.4 (carbon bound to Re); -128.7 (*o*- or *m*-); -124.3 (*p*-)
$CH_3CORe(CO)_5$	-183.0	-181.2	7	-244.0 (C=O); -57.2 (CH_3)
$C_6H_5CORe(CO)_5$	-182.9	-181.0	6	-245.4 (C=O); -154.6 (*C*-CO); -130.8 (*p*-); -128.3 (*o*- or *m*-); -126.2 (*o*- or *m*-)
$BrRe(CO)_5$[d]	-177.8	-176.3	10	
$[(CH_3CN)Re(CO)_5][PF_6]$[e]	-178.6	-179.6	6	-128.1 (CN); -4.3 (CH_3)

[a]Chemical shifts in p.p.m. relative to tetramethylsilane; $CDCl_3$ solvent except as noted.

[b]Line width at half height in Hz for *cis* carbonyl signal.

[c]See text

[d]Spectrum of lower quality due to low solubility; lower precision in δCO(*trans*).

[e]CD_3CN solvent.

(a) Resonances due to carbon atoms other than carbonyl carbon atoms

Few examples of ^{13}C NMR chemical shifts for acyl carbon atoms bound to transition metals have been reported. The values of -245.4 and -244.0 p.p.m. found for $C_6H_5CORe(CO)_5$ and $CH_3CORe(CO)_5$ are shifted up-field with respect to the iron derivative $(\eta\text{-}C_5H_5)Fe(CO)_2COCH_3$ for which the chemical shift of the acyl carbon atom is -254.4 p.p.m.[89] It would therefore be of interest to obtain the spectra of $C_6H_5COMn(CO)_5$ and $CH_3COMn(CO)_5$ to compare closely related compounds within one transition metal group.

The molecule $C_6H_5Re(CO)_5$ represents one of the few reports of phenyl carbon resonances due to a phenyl group σ-bonded to a transition metal, other examples being $(\eta\text{-}C_5H_5)_2TiPh_2$, *cis*-$[PtPh_2(PEt_3)_2]$, *trans*-$[PtPh_2(PEt_3)_2]$ and $[PtPh_2Cl_2(PEt_3)_2]$.[90] Carbonyl resonances for the complexes $(\eta\text{-}C_5H_5)Fe(CO)_2X$ (X = C_6H_5, p-C_6H_4Cl, C_6F_5) have been reported,[91] but the phenyl carbon resonances were omitted. Phenyl resonances for $C_6H_5Re(CO)_5$ could be assigned on a relative intensity basis, the weakest signal being due to the carbon atom bound to rhenium (this carbon atom has no hydrogen atom attached to it and does not benefit from Overhauser enhancement in a proton-decoupled spectrum). The *para*-carbon signal is of intermediate intensity and the two pairs of *ortho*- and *meta*-carbon atoms give the strongest

signals. The phenyl resonances in $C_6H_5CORe(CO)_5$ were similarly assigned and are also listed in Table XVI. These assignments were confirmed using proton coupled spectra. All of the phenyl carbon resonances showed small long-range couplings to hydrogen atoms on the phenyl ring, but carbon atoms directly bound to hydrogen were in addition split into widely separated doublets ($^1J_{(^1H-^{13}C)}$ values were of the order of 160 Hz).

The resonance of the methyl carbon in $CH_3Re(CO)_5$ lies to high field of TMS at +38.0 p.p.m. It is also more highly shielded than that in $CH_3Mn(CO)_5$ which occurs at +212.2 p.p.m. relative to CS_2[92] (+19.4 p.p.m. relative to TMS), and is in fact the highest field resonance of this type yet reported.[90] The most highly shielded example previously observed was the methyl carbon resonance of $(\eta\text{-}C_5H_5)W(CO)_3CH_3$ which occurs at +28.9 p.p.m.[89]

In the complexes $(CH_3)_3SnRe(CO)_5$ and $(CH_3)_3PbRe(CO)_5$ couplings from the Group IV atoms to the methyl carbon atoms were observed. In the former case, even though an excellent spectrum of the carbonyl region was obtained, tin coupling to carbonyl carbon atoms was not observed. The coupling constants noted in Table XVI are rather similar to values found in this laboratory for the complexes *cis*-$Ru(CO)_4[Sn(CH_3)_3]_2$ and *cis*-$Ru(CO)_4[Pb(CH_3)_3]_2$.[93]

(b) Resonances due to carbonyl carbon atoms

Most of the complexes studied gave satisfactory spectra in the carbonyl region at ambient temperatures (see Table XVI); $(CH_3)_3PbRe(CO)_5$ was a notable exception. Even at -20°C in toluene-d_8 only a broad singlet (half-width *ca.* 25 Hz) was observed and this became even broader at temperatures up to 70°C. The large half-width value over the wide temperature range employed suggests that quadrupole broadening and not stereochemical nonrigidity produces the observed line broadening. It therefore appears that lower temperatures will have to be employed to obtain a satisfactory spectrum of this complex. This behaviour can be contrasted with that of $(CH_3)_3GeRe(CO)_5$ and $CH_3Re(CO)_5$, in which the carbonyl peaks remain clearly resolved at elevated temperatures. Line widths observed for the carbonyls *cis* to the substituents in these complexes are 14 Hz and 11 Hz respectively in toluene-d_8 at 100°C. Thus quadrupole broadening is not a serious problem for these complexes. The sharply resolved spectrum of $CH_3CORe(CO)_5$ is shown in Figure 25.

A great deal of the discussion of ^{13}C NMR chemical shift values for carbonyl carbon atoms has centered around their correlation with CK carbonyl stretching force constants.[73] In attempting a similar treatment of our own results, several interesting features have been noted.

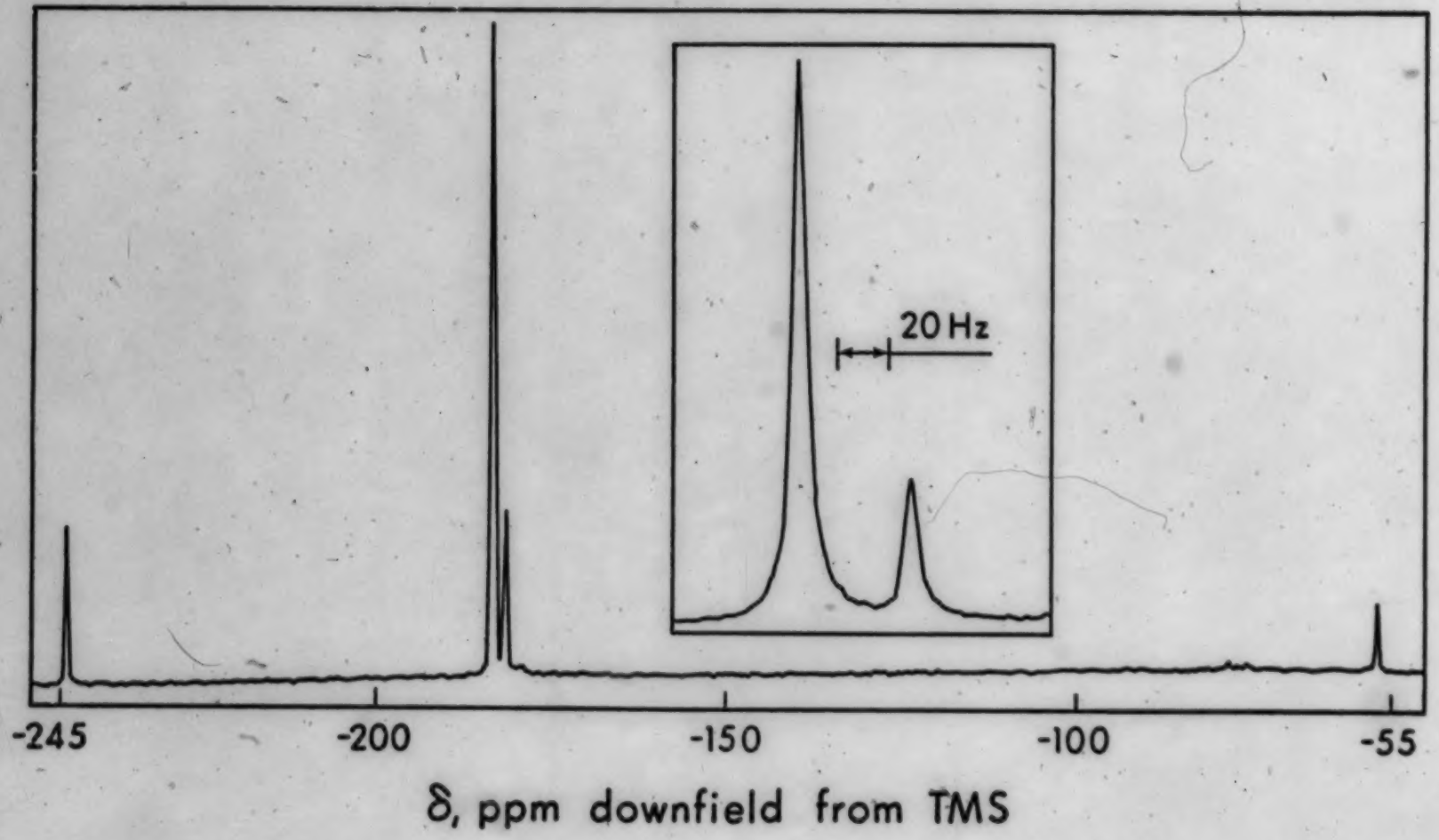

Figure 25. ^{13}C NMR spectrum of $CH_3CORe(CO)_5$ in $CDCl_3$.

In the following discussion of neutral mono-substituted metal carbonyl derivatives of the types $LM(CO)_5$, (M = Cr, W), and $XRe(CO)_5$, the four equivalent carbonyl ligands *cis* to L or X and the unique carbonyl group *trans* to L or X will be designated "*cis*" and "*trans*" respectively. The assignment of *cis* and *trans* carbonyl resonances in these systems is straightforward on the basis of relative peak intensities.

For the neutral mono-substituted rhenium carbonyl derivatives listed in Table XVI it can be seen that the *trans* carbonyl resonance is up-field from (i.e., more shielded than) the *cis* carbonyl resonance. This phenomenon has been confirmed elsewhere for two rhenium derivatives[88] and has also been observed for a related manganese complex.[88] In contrast, complexes of the type $LW(CO)_5$[94,21] and $LCr(CO)_5$[21,95] give spectra in which the *trans* carbonyl resonance is always down-field from (i.e., more deshielded than) the *cis* carbonyl resonance. The significance of this reversal of shielding of *cis* and *trans* carbonyls is apparent when it is considered that the force constant of the *trans* carbonyl is always lower than that of the *cis** (Table XVII). Thus it follows

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*In octahedral complexes of this type $k_1 < k_2$ in all known instances. Previous force constant value for $Ph_3GeMn(CO)_5$ and $Ph_3SnMn(CO)_5$[96] are incorrect due to a wrong assignment. Correct energy factored values for $Ph_3GeMn(CO)_5$ are $k_1 = 16.40$, $k_2 = 16.71$, while those for $Ph_3SnMn(CO)_5$ are 16.34 and 16.66 mdyn/Å.[97] These compounds are thus not exceptions to the generalization that $k_1 < k_2$.

TABLE XVII

CARBONYL STRETCHING FREQUENCIES AND COTTON-KRAIHANZEL FORCE CONSTANTS FOR PENTACARBONYLRHENIUM COMPLEXES

Compound	Stretching Frequencies[a] (cm^{-1})			Cotton-Kraihanzel Force Constants[b] (mdyn/Å)		
	$A_1^{(2)}$	E	$A_1^{(1)}$	k_1	k_2	k_i
$Cl_3SiRe(CO)_5$[c]	2140	2038	2030	16.80	17.30	0.26
$(CH_3)_3SiRe(CO)_5$[c]	2112	2001	2001	16.36	16.72	0.28
$(CH_3)_3GeRe(CO)_5$	2111	2002	1995	16.24	16.73	0.27
$(CH_3)_3SnRe(CO)_5$[d]	2108	2003	2003	16.38	16.73	0.26
$(CH_3)_3PbRe(CO)_5$	2106	2003	1994	16.22	16.72	0.26
$CH_3Re(CO)_5$	2125	2013	1983	16.03	16.94	0.29
$C_6H_5Re(CO)_5$	2131	2020	1988	16.11	17.05	0.29
$CH_3CORe(CO)_5$	2131	2017	2000	16.32	17.01	0.29
$C_6H_5CORe(CO)_5$	2133	2021[e]	2000	16.31	17.07	0.29
$BrRe(CO)_5$[f]	2151	2044	1985	16.03	17.44	0.28
$[(CH_3CN)Re(CO)_5][PF_6]$	2170	2066	2031	16.80	17.79	0.27

[a] All spectra recorded in *cyclo*hexane, except $[(CH_3CN)Re(CO)_5][PF_6]$ in CH_2Cl_2.

[b] k_1 = force constant of *trans* carbonyl, k_2 = force constant of *cis* carbonyls.

[c] Stretching frequencies taken from Ref. 64.

[d] Stretching frequencies taken from Ref. 60.

[e] E mode split into two peaks of nearly equal intensity at 2025 and 2017 cm^{-1}. Mean value used in calculations.

[f] Stretching frequencies taken from Ref. 101.

that in a given molecule one can make no prediction as to whether the *cis* or *trans* carbonyl will be more shielded on the basis of CK carbonyl stretching force constants.

In complexes of the type *cis*-$X_2M(CO)_4$, where X is H[98] or a Group IV ligand,[93] and M = Fe, Ru, Os, the resonances of carbonyl carbon atoms *trans* to X are also found to be more shielded than those of the *cis* carbonyl carbons.

Little work has been done on mono-substituted derivatives of manganese pentacarbonyl. However, it does appear that the generally observed[73] large increase in shielding of carbonyl carbon resonances upon descending a transition metal group is in evidence here. The ^{13}C NMR spectrum of $CH_3Mn(CO)_5$ in the carbonyl region exhibits a broad, unresolved singlet at -21 p.p.m. relative to CS_2[92] (-214 p.p.m. relative to TMS), and that of $C_6H_5CH_2Mn(CO)_5$ at -87°C shows two signals at -211.1 and -209.1 p.p.m. due to *cis* and *trans* carbonyls respectively.[88] These values can be compared with those of -185.2 and -181.3 p.p.m. for the *cis* and *trans* carbonyls of $CH_3Re(CO)_5$. As has been mentioned previously[94,21] such a large up-field shift when descending a group cannot be explained in terms of carbonyl stretching force constants.

To apply the usual treatment of experimental data to our own results a plot of Cotton-Kraihanzel carbonyl stretching force constants *vs.* ^{13}C chemical shifts is shown in Figure 26. It can immediately be seen that for the *cis*

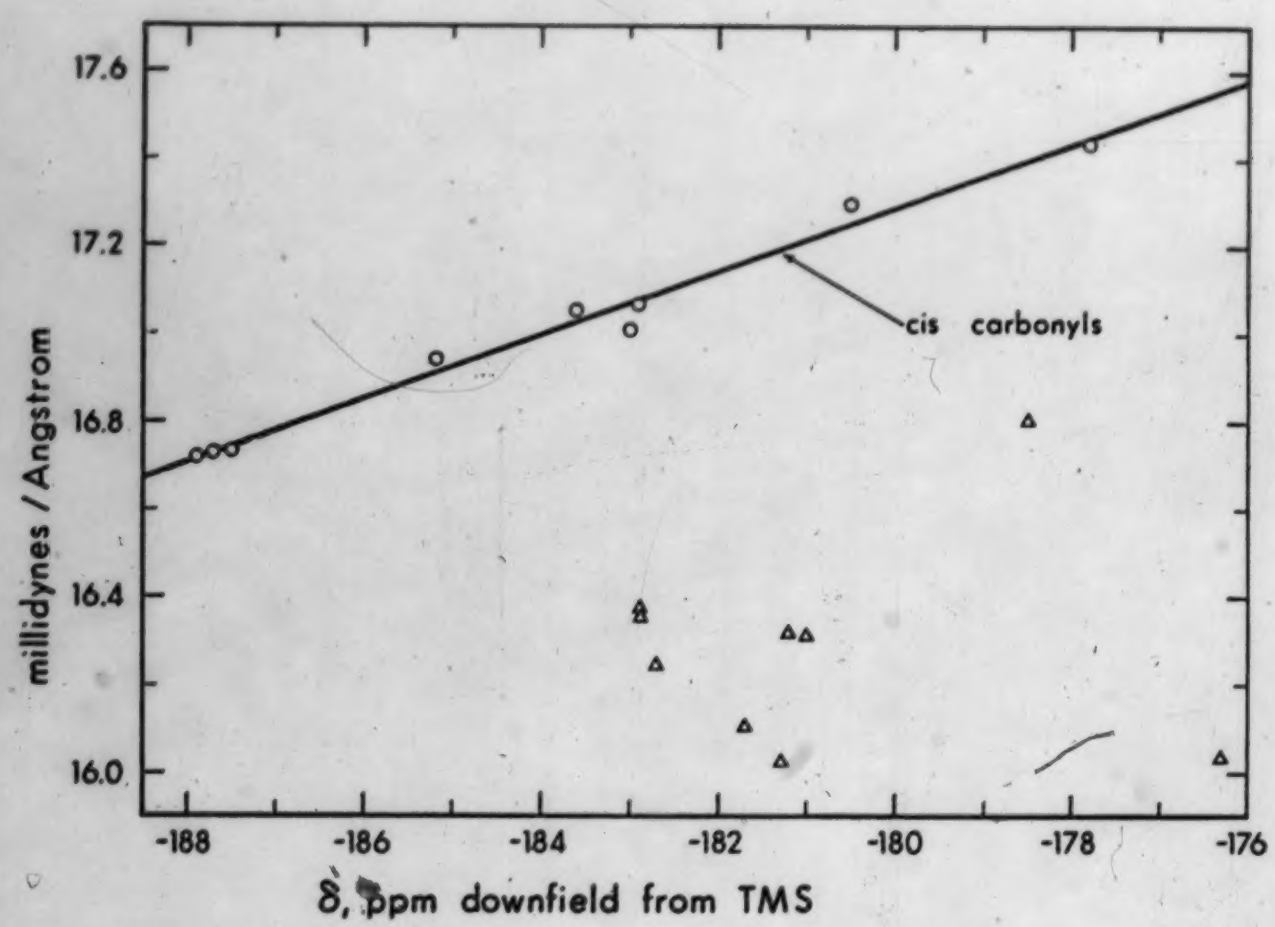

Figure 26. A plot of Cotton-Kraihanzel carbonyl force constants *vs.* ^{13}C chemical shifts for a series of rhenium pentacarbonyl complexes.

carbonyl carbon atoms an excellent correlation exists, with more highly shielded carbonyl carbon atoms belonging to ligands of higher force constants. It should be noted in this connection that points reported[94] for the *cis* carbonyls of complexes $LW(CO)_5$ fall on a continuation of the same straight line. However, the correlation for the *trans* carbonyl groups is poor, a phenomenon which has previously been noted for a series of carbene derivatives of chromium carbonyl.[21] Thus changing chemical shifts of *trans* carbonyl carbon atoms are not always reflected by changes in carbonyl force constants.

The Ionic Complex $[(CH_3CN)Re(CO)_5][PF_6]$

A good spectrum of this compound was obtained at ambient temperature in CD_3CN solvent (see Table XVI). The data will be discussed in terms of non-carbonyl and carbonyl carbon atoms as before.

(a) Resonances due to carbon atoms other that carbonyl carbon atoms

Peaks due to cyanide carbon atoms were observed at -128.1 p.p.m. and -118.3 p.p.m., and these were assigned to co-ordinated CH_3CN and to CD_3CN solvent, respectively. The absence of solvent exchange at ambient temperature was confirmed by a further experiment in which a small amount of

CH_3CN was added to the solution. As well as the septet due to the CD_3 carbon of CD_3CN, two CH_3 singlets were observed at -4.3 and -1.6 p.p.m. The former resonance was that of the complexed CH_3CN group, the latter that of the free CH_3CN in solution. The spectrum was essentially unchanged at 70°. Hence any exchange between the two is slow on the NMR time-scale.

(b) Resonances due to carbonyl carbon atoms

It is interesting to note that the *trans* carbonyl resonance is down-field from the *cis* resonance in this case (see Table XVI), in contrast to all the neutral rhenium derivatives discussed earlier. In this sense the spectrum resembles those of neutral complexes of the type $LM(CO)_5$ (M = Cr, Mo, W) where, in all cases reported so far, the *trans* resonance is down-field from the *cis*.[73] The reason why the $[(CH_3CN)Re(CO)_5]^+$ salt shows such different behaviour from the neutral $XRe(CO)_5$ species is not clearly understood at present. However, it is important to note that the reversal cannot be explained in terms of force constants since the *cis* carbonyl force constants are higher that those of the *trans* carbonyl in all cases (see Table XVII).

As can be readily seen the data for the *cis* carbonyl force constant and chemical shift will not produce a point on the straight line in Figure 26. The significance of

this is hard to interpret at the moment since changes in the solvents used for IR and NMR studies relative to the neutral $XRe(CO)_5$ derivatives may be at least partly responsible. It should also be noted here that the carbonyl resonances for $[(CH_3CN)Re(CO)_5][PF_6]$ remain well resolved in CD_3CN at 70°C. In view of the interesting features observed for this compound it is hoped that further cationic rhenium species of the type $[LRe(CO)_5]^+$ will be studied.

EXPERIMENTAL

Compounds were prepared according to the methods in the references indicated: $CH_3Re(CO)_5$, $CH_3CORe(CO)_5$, $C_6H_5Re(CO)_5$ and $C_6H_5CORe(CO)_5$ were prepared by the method of Hieber *et al.*[87] The sodium salt of $Re_2(CO)_{10}$ was used.

Displacement reactions using $Na^+Re(CO)_5^-$ were used in the preparation of $(CH_3)_3GeRe(CO)_5$, $(CH_3)_3SnRe(CO)_5$,[60] and $(CH_3)_3PbRe(CO)_5$. Details of the synthesis and characterisation of the germanium compound were described in Chapter II. The preparation of the lead compound has very recently been reported[99] and the infrared bands are in excellent agreement; the compound is colourless when pure, however. Samples of $Cl_3SiRe(CO)_5$[100] and $(CH_3)_3SiRe(CO)_5$[64] prepared by the reaction of $Re_2(CO)_{10}$ with Cl_3SiH and $(CH_3)_3SiH$ were kindly supplied by Dr. W. Jetz. The method of Kaesz *et al.*[101] was used in the preparation of $BrRe(CO)_5$ and $ClRe(CO)_5$; a sample of the former was supplied by Dr. D. Dong.

^{13}C NMR spectra were recorded using the Fourier transform pulsed NMR technique, as described in Chapter VI. Proton-decoupling was employed in complexes containing hydrogen atoms, except as noted in the discussion. The number of scans was typically in the range 1,000 to 4,000. Spectra of neutral complexes were recorded in $CDCl_3$ at ambient temperatures (45°C for the Varian HA 100, 35°C for

the Bruker HFX-90), except as noted in the text. The salt $[(CH_3CN)Re(CO)_5][PF_6]$ was prepared as described by Okamoto[102] from $Re_2(CO)_{10}$ and $NOPF_6$ in CH_3CN solvent, and its spectrum was recorded in CD_3CN. Solution concentrations were generally of the order of 0.5 M, although somewhat higher in a few cases. ^{13}C chemical shifts were measured relative to the internal solvent resonance and are reported relative to TMS by use of the relations $\delta(TMS) = \delta(CDCl_3) - 77.035$ p.p.m. and $\delta(TMS) = \delta(\underline{C}D_3CN) - 1.187$ p.p.m.

Infrared spectra were recorded as described in Chapter II, and reported bands are considered accurate to ± 1 cm^{-1}. *Cyclo*hexane was employed as solvent for all neutral complexes, and dichloromethane was used for $[(CH_3CN)Re(CO)_5][PF_6]$. Approximate force constants were calculated using the Cotton-Kraihanzel approximation.[103] In cases where infrared band positions not measured in this work were employed in force constant calculations, references are given in the footnotes to Table XVII. In such cases force constants were recalculated from the published data to ensure internal consistency.

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APPENDIX I

FRACTIONAL COORDINATES OF ATOMS IN $[Me_2GeRe(CO)_4COMe]_2$*

(Data provided by L. Y. Y. Chan, 1974)

Note: These values differ, in the following respects, from those deposited as Supplementary Data with *J. Am. Chem. Soc.*, 96, 5931 (1974): (1) Final R. is now 3.6%; (2) hydrogen atom positions are given; (3) thermal parameters are given.

Atom	*x*	*y*	*z*	B(Å^{-1})
Re	0.20207(8)	0.11310(7)	-0.14571(7)	a
Ge	0.0526(2)	0.2187(2)	-0.0016(2)	b
C 1	0.292(2)	0.029(2)	-0.261(2)	5.26(52)
O 1	0.354(2)	-0.019(3)	-0.328(2)	7.78(46)
C 2	0.306(2)	0.031(2)	-0.009(2)	3.88(42)
O 2	0.367(1)	-0.024(2)	0.071(1)	4.96(33)
C 3	0.101(3)	0.199(2)	-0.271(2)	5.30(47)
O 3	0.033(2)	0.253(2)	-0.347(2)	6.53(37)
C 4	0.343(3)	0.237(2)	-0.126(2)	4.44(42)
O 4	0.414(2)	0.311(2)	-0.110(2)	7.23(41)

APPENDIX I (continued)

Atom	x	y	z	B(Å^{-1})
C 5	0.045(2)	-0.017(3)	-0.144(2)	3.51(38)
O 5	0.061(2)	-0.101(1)	-0.069(1)	3.52(24)
C 6	0.132(3)	0.308(2)	0.135(2)	5.12(50)
C 7	-0.144(3)	0.304(2)	-0.067(2)	4.54(45)
C 8	-0.088(2)	0.018(3)	-0.226(2)	3.98(42)
H 1	0.21	0.260	0.175	6.3
H 2	0.069	0.318	0.196	6.3
H 3	0.167	0.381	0.118	6.3
H 4	-0.110	0.370	-0.120	6.3
H 5	-0.165	0.330	-0.008	6.3
H 6	-0.173	0.252	-0.122	6.3
H 7	-0.070	0.007	-0.309	6.3
H 8	-0.118	0.097	-0.218	6.3
H 9	-0.171	-0.030	-0.219	6.3

APPENDIX I (continued)

[$\beta \times 10^5$]	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
[a] Re	706(10)	585(7)	823(8)	- 3(8)	158(6)	78(6)
[b] Ge	680(23)	472(15)	774(17)	-21(13)	-17(21)	-36(15)

* Standard deviation of last digit given in parenthesis